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ABSTRACT

This technical specialty course is one of thirty-five courses designed for use by two-year postsecondary institutions in five nuclear technician curriculum areas: (1) radiation protection technician, (2) nuclear instrumentation and control technician, (3) nuclear materials processing technician, (4) nuclear quality-assurance/quality-control technician, and (5) nuclear reactor (plant) operator trainee. This course, Nuclear Chemical Processes, contains seven modules: Head-End Treatment, Ion Exchange, Solvent Extraction, Precipitation Techniques and Centrifugation, Techniques of Chemical Concentration, Diffusion and Enrichment Process, and Nuclear Waste Handling Processes. Each module follows a typical format including the following sections: introduction, module prerequisites, objectives, subject matter, exercises, materials, procedures, data tables, reference materials, and tests. (A master index and suggested program planning guides are also available. See CE 026 856 and CE 026 639-643.) (LRA)

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ED192105

Nuclear Technology Series

COURSE 23

NUCLEAR CHEMICAL PROCESSES

CENTER FOR OCCUPATIONAL RESEARCH
AND DEVELOPMENT, INC.
4800 LAKEWOOD DRIVE
WACO, TEXAS 76710

CE 026 663

U S DEPARTMENT OF HEALTH
EDUCATION & WELFARE
NATIONAL INSTITUTE OF
EDUCATION

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PREFACE

ABOUT NUCLEAR TECHNOLOGY MODULES

The modules – developed for use in two-year postsecondary technical institutions to prepare technicians for employment – are useful in industry for updating employees in company-sponsored training, and as laboratory texts in engineering schools. The principles, techniques and skills taught in the modules, based on tasks that nuclear technicians perform, were obtained from a nationwide advisory committee of employers of nuclear technicians. Each module was written by a working technical expert/experienced writer team and tested with students.

A module contains the following elements:

Introduction, which identifies the topic and often includes a rationale for studying the material.

Module Prerequisites, which identify the material a student should be familiar with before studying the module.

Objectives, which clearly identify what the student is expected to know for satisfactory module completion. The objectives, stated in terms of action-oriented behaviors, include such action words as operate, measure, calculate, identify and define, rather than words with many interpretations, such as know, understand, learn and appreciate.

Subject Matter, which presents the background theory and techniques supportive to the objectives of the module. Subject matter is written with the technical student in mind.

Exercises, which provide practical problems to which the student can apply this new knowledge.

Materials, which identify the equipment required to complete the laboratory procedure.

Procedures, which is the experiment section, or "hands-on" portion of the module (including step-by-step instruction) designed to reinforce student learning.

Data Tables, which are included in most modules for the first year (or basic) courses to help the student learn how to collect and organize data.

Reference Materials, which are included as suggestions for supplementary reading/viewing for the student.

Test, which measures the student's achievement of the prestated objectives.

A helpful Index has been added at the end of each course.

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The Nuclear Technology Series consists of five curricula:

- Nuclear Reactor (Plant) Operator Trainee.
- Radiation Protection Technician.
- Nuclear Materials Processing Technician.
- Nuclear Quality-Assurance/Quality-Control Technician.
- Nuclear Instrumentation and Control Technician.

The completed Nuclear Technology Series consists of the following 35 technical specialty courses:

- Radiation Physics.
- Radiation Protection I.
- Principles of Process Instrumentation.
- Heat Transfer and Fluid Flow.
- Introduction to Nuclear Systems.
- Instrumentation and Control of Reactors and Plant Systems.
- Reactor Operations.
- Reactor Safety.
- Reactor Auxiliary Systems.
- Power Plant Systems.
- Radiation Detection and Measurement.
- Reactor Physics.
- Power Plant Chemistry.
- Introduction to Quality Assurance/Quality Control.
- Metallurgy and Metals Properties.
- Mechanical Component Characteristics and Specifications.
- Radiation Protection II.
- Radiological Emergencies.
- Radiation Shielding.
- Radiation Monitoring Techniques (Radiochemical).
- Radioactive Materials Disposal and Management.
- Advanced Radionuclide Analysis.
- Nuclear Chemical Processes.
- Nuclear Systems and Safety.
- Radioactive Material Handling Techniques.
- Nondestructive Examination (NDE) Techniques I.
- Metrology.
- Welding Inspection.
- Civil/Structural Inspection.
- Mechanical Inspection.
- Quality-Assurance Practices.
- Nondestructive Examination (NDE) Techniques II.
- Control Systems I.
- Control Systems II.
- Power Plant Electrical Systems and Components.

Availability: Instructional modules are available individually or by courses from:

Center for Occupational Research and Development
4800 Lakewood Drive, Suite 5
Waco, Texas 76710
Telephone (817) 772-8756

Printed:

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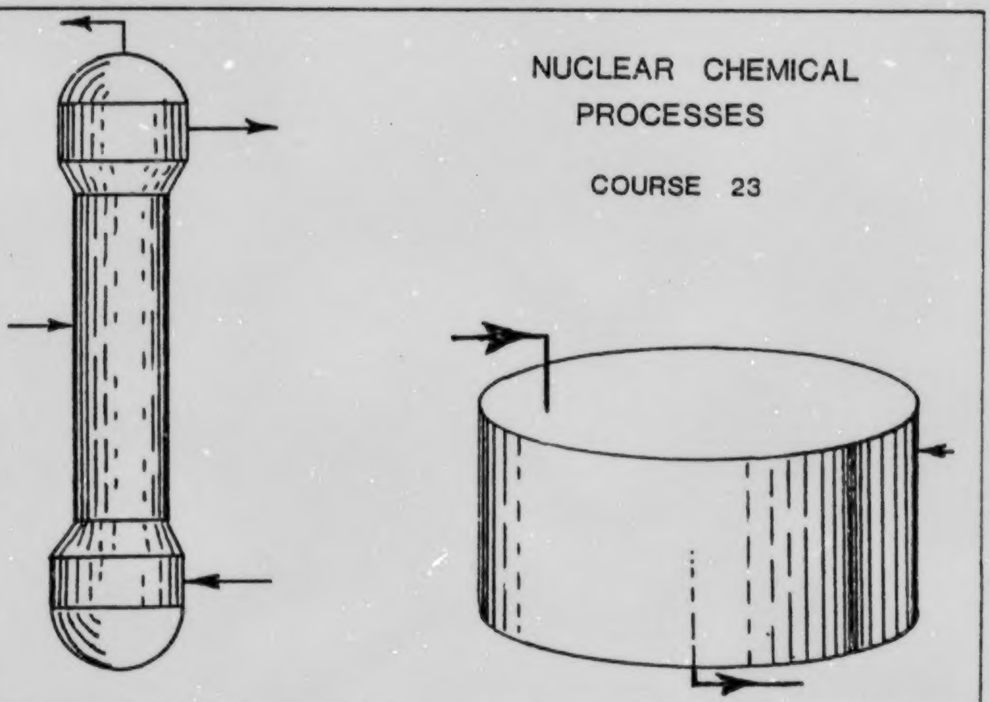
MODULE 23-4 Precipitation Techniques and Centrifugation
MODULE 23-5 Techniques of Chemical Concentration
MODULE 23-6 Diffusion and Enrichment Process
MODULE 23-7 Nuclear Waste Handling Processes

NUCLEAR TECHNOLOGY

MODULE 23-1

HEAD-END TREATMENT



NUCLEAR CHEMICAL PROCESSES

COURSE 23

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

⇨ MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

In 1977, President Carter suspended indefinitely the reprocessing of spent fuel, pending an international review of nuclear proliferation issues. At present (February, 1980), there are no properly licensed sites for the safe disposal of radioactive waste products from a reprocessing complex. When reprocessing is resumed, however, the process will be of the traditional type described in this module and as outlined in the remainder of this Introduction.

Since the fissioning of nuclear fuels produces radioactive neutron absorbers that inhibit the fission chain reaction, the fuel must be removed periodically from the reactor and the valuable components recovered for recycling. The fuel must be removed, stored, packed, shipped to a reprocessing facility, unloaded, disassembled, and reprocessed. The recovered fissile materials then are returned to a refabrication or enrichment facility and finally sent back to a nuclear reactor for further use. Figure 23-1-1 depicts this process – the nuclear fuel cycle.

This module introduces the use of nuclear fuels in reactors and describes the "head-end" portion of the nuclear fuel cycle – the unloading and disassembly of the fuel assemblies at a spent-fuel reprocessing plant. It is the first of a series of modules that describes nuclear chemical processes for the reprocessing of nuclear fuel. This module includes a generalized description of nuclear reactors, nuclear fuel assemblies, the shipping and storage of nuclear fuels, and the activities of a commercial nuclear-fuel reprocessing plant.

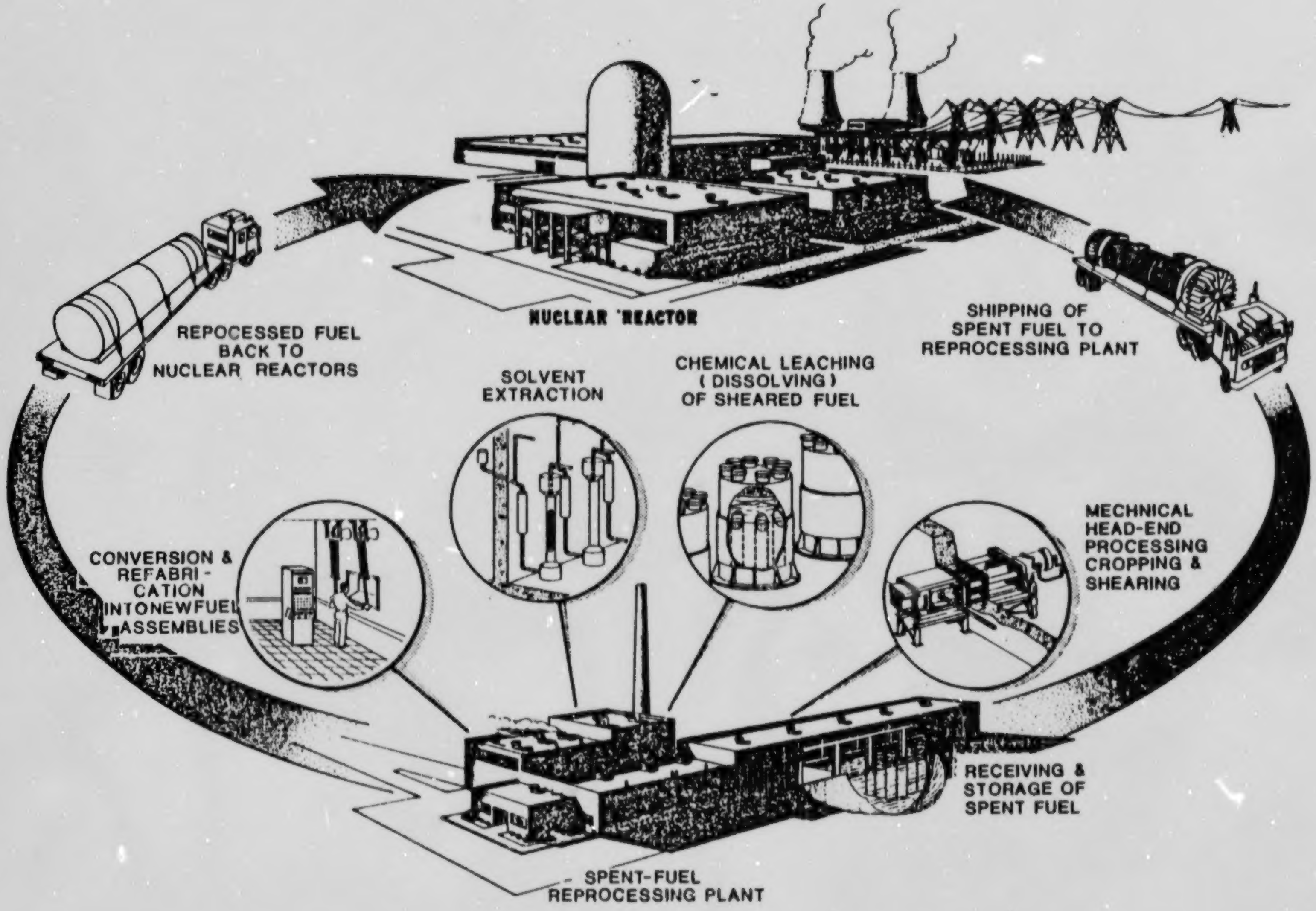

NUCLEAR REACTOR
SHIPPING OF SPENT FUEL TO REPROCESSING PLANT
REPOCESSED FUEL BACK TO NUCLEAR REACTORS
SOLVENT EXTRACTION
CHEMICAL LEACHING (DISSOLVING) OF SHEARED FUEL
MECHNICAL HEAD-END PROCESSING CROPPING & SHEARING
CONVERSION & REFABRICATION INTO NEW FUEL ASSEMBLIES
RECEIVING & STORAGE OF SPENT FUEL
SPENT-FUEL REPROCESSING PLANT

Figure 23-1-1. Generalized nuclear fuel cycle of the United States.

MODULE PREREQUISITES

The student should have completed a course in basic algebra and should have a working knowledge of nuclear chemical terms and processes.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. List and discuss basic steps in yellowcake and uranium hexafluoride production.
2. Describe the gaseous diffusion process.
3. Describe the fabrication of fuel assemblies.
4. Describe the design characteristics of a spent-fuel shipping cask.
5. Describe a typical spent-fuel receiving and storage facility.
6. Draw a flow chart of typical major head-end reprocessing steps.
7. Describe, with the aid of labeled drawings of a fuel storage basin and a typical mechanical cell, the preparation of fuel for reprocessing. Include descriptions of the interface with the downstream solvent-extraction process.
8. Describe fire safety, criticality, and accountability features of the head-end process.

NUCLEAR REACTORS AND THEIR FUEL

Nuclear reactors allow fission to be initiated and maintained at a controlled rate in a self-supporting chain reaction. A reactor consists of fissile material, usually uranium enriched to 2-4% ^{235}U, a control system that initiates and controls the fission chain reaction, a coolant that removes heat, and various structural materials and shielding.

Almost all power reactors in the United States are light water power reactors: the reactor coolant ordinarily is water. The two types of water reactors are –

- The pressurized water reactor (PWR).
- The boiling water reactor (BWR).

The PWR (Figure 23-1-2) is cooled by water under pressure. The water is heated as it is pumped through the core but does not boil since it is pressurized. This heated water is pumped to the steam generator, where it transfers heat to the water there to produce steam that is piped to the turbine.

In the BWR reactor (Figure 23-1-3), however, the coolant water boils inside the reactor, and the resulting steam is piped to the turbine.

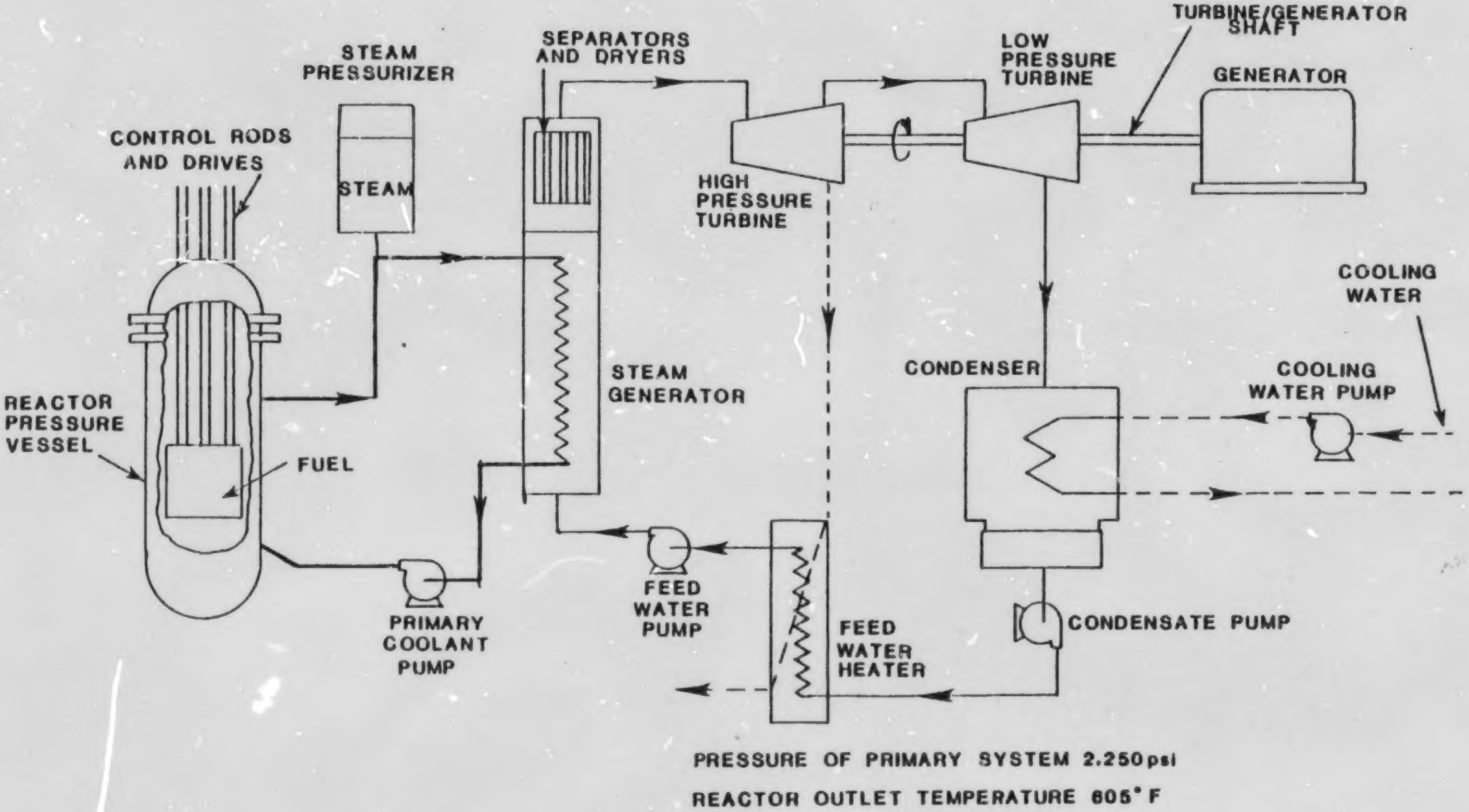
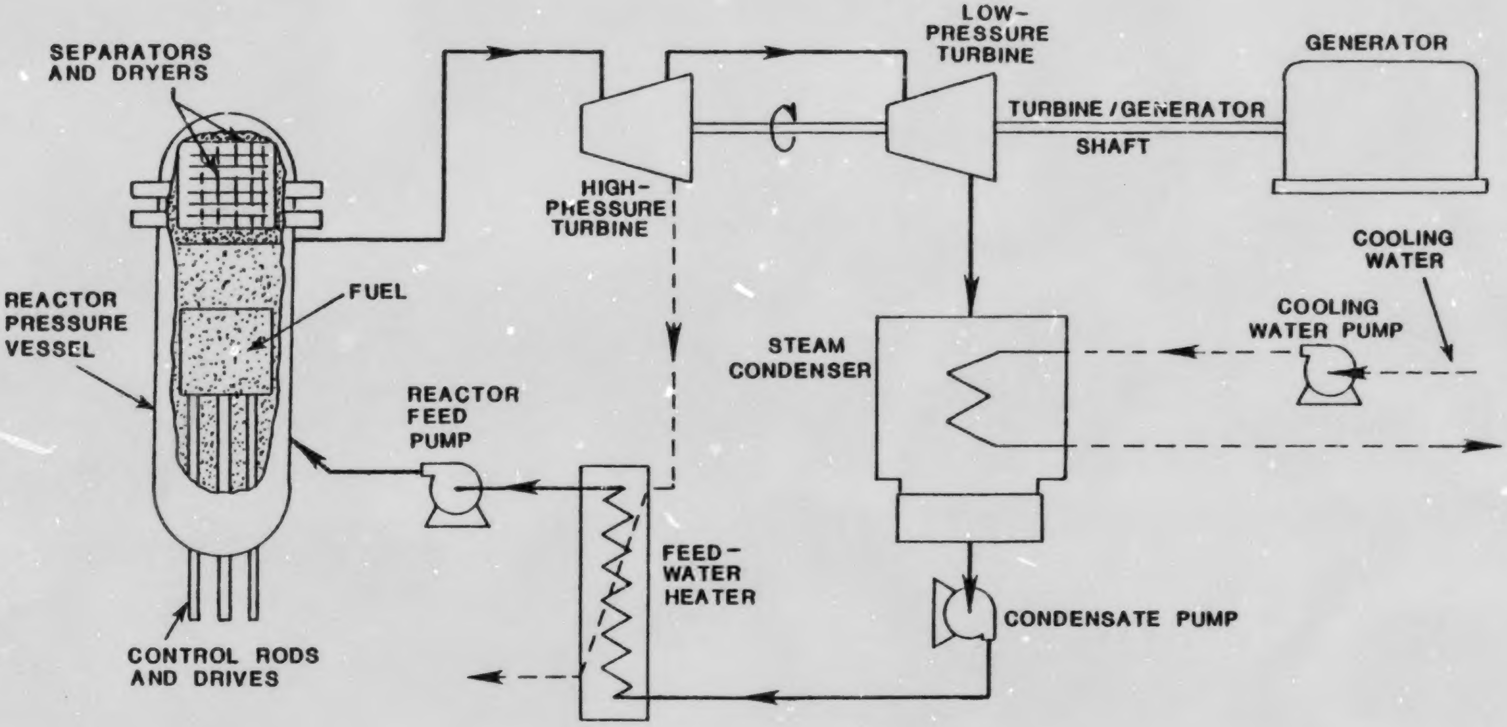

TURBINE/GENERATOR SHAFT
SEPARATORS AND DRYERS
STEAM PRESSURIZER
LOW PRESSURE TURBINE
GENERATOR
CONTROL RODS AND DRIVES
STEAM
HIGH PRESSURE TURBINE
COOLING WATER
CONDENSER
COOLING WATER PUMP
STEAM GENERATOR
REACTOR PRESSURE VESSEL
FUEL
FEED WATER PUMP
PRIMARY COOLANT PUMP
CONDENSATE PUMP
FEED WATER HEATER
PRESSURE OF PRIMARY SYSTEM 2.250 psi
REACTOR OUTLET TEMPERATURE 605° F

Figure 23-1-2. Pressurized water reactor power plant.


SEPARATORS AND DRYERS
REACTOR PRESSURE VESSEL
FUEL
CONTROL RODS AND DRIVES
REACTOR FEED PUMP
HIGH-PRESSURE TURBINE
LOW-PRESSURE TURBINE
GENERATOR
TURBINE / GENERATOR SHAFT
COOLING WATER
COOLING WATER PUMP
STEAM CONDENSER
FEED-WATER HEATER
CONDENSATE PUMP

PRESSURE OF PRIMARY SYSTEM 1000 psi
REACTOR OUTLET TEMPERATURE 550° F

Figure 23-1-3. Boiling water reactor power plant.

In the United States, slightly enriched uranium-235 is used as fuel for these reactors. A number of steps are required in the preparation of uranium for use in a reactor. These steps include milling to extract uranium from the mined ore, refining and conversion to UF_6, enrichment, conversion to UO_2 pellets and fabrication of fuel assemblies (Figure 23-1-4).

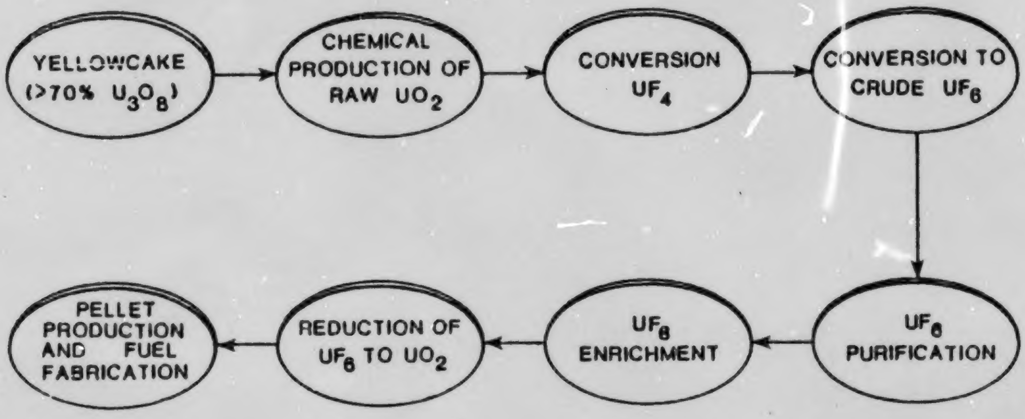

YELLOWCAKE ($>70\%$ U_3O_8)
CHEMICAL PRODUCTION OF RAW UO_2
CONVERSION UF_4
CONVERSION TO CRUDE UF_6
UF_6 PURIFICATION
UF_6 ENRICHMENT
REDUCTION OF UF_6 TO UO_2
PELLET PRODUCTION AND FUEL FABRICATION

Figure 23-1-4. Process chart for UF_6 production.

The uranium mill extracts uranium from the ore by crushing it, leaching it with an acid or alkaline to dissolve the uranium, and then recovering the uranium from the solution by solvent extraction or ion-exchange techniques. This process results in "yellowcake," a uranium concentrate that contains from 70 to 90% U_6O_8.

The uranium in yellowcake is converted to uranium hexafluoride (UF_6) by various chemical processes. The UF_6 then is enriched to the required concentration of the fissionable isotope, ^{235}U, in a gaseous diffusion plant. The plant separates isotopes through utilization of the principles of gas kinetics. The diffusion apparatus consists of hundreds of chambers, each divided into two compartments by a porous membrane barrier that has an average pore size of approximately five microns. (Refer to Figure 23-1-5.) A pressure differential is established across the barrier to increase the speed with which the molecules will diffuse through the barrier. Because the lighter molecule of $^{235}UF_6$ will travel faster than the heavier $^{238}UF_6$ molecule, the two gaseous isotopes can be separated to a degree, as the lighter $^{235}UF_6$ will travel faster through the membrane. This process must be repeated several times to achieve the desired degree of UF_6 enrichment.

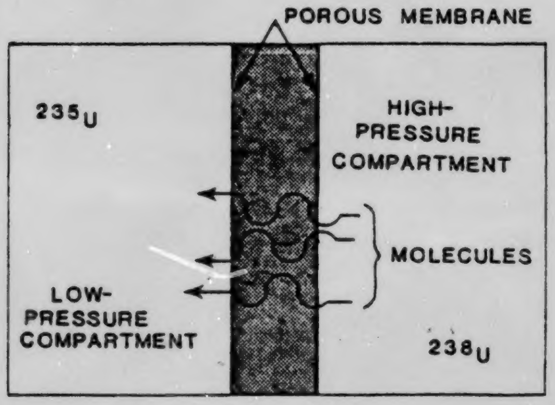


Figure 23-1-5. Gaseous diffusion process.

The gas that passes through the barrier is richer in the lighter isotope (^{235}U), and that remaining behind has a higher proportion of the heavier isotope (^{238}U).

This process of diffusion must be repeated many times before practical enrichment is possible; consequently, a gaseous diffusion plant consists of hundreds of similar stages ("diffusion cascades"). In each stage, a pump compresses the gas to the next stage pressure, where a cooler removes the generated heat of compression. The gas becomes more enriched as it travels up the cascade, and the degree of enrichment depends upon the number of stages in the overall system. Depleted uranium (known as "tails") is withdrawn at the bottom of the cascade.

Gaseous diffusion plants are located at Oak Ridge, Tennessee; Paducah, Kentucky; and Portsmouth, Ohio.

The enriched UF_6 is converted into UO_2 and the raw UO_2 reduced to the desired particle size. These particles are pelletized to high pressure and ground to a proper diameter. The pellets are arranged in a proper stack length, checked for uranium content, and inserted into a thin-walled Zircaloy tube (Figure 23-1-6). One end of the tube is capped and welded, helium introduced into the tube, and the other end capped and welded. Such tubes are assembled and bound together with other components to form an assembly (Figure 23-1-7).

All fuel assemblies of a PWR are mechanically identical and are installed vertically on the core support plate in the reactor vessel. The number of assemblies, rods in an assembly, and fuel length vary by vendors and weigh up to 500 pounds.

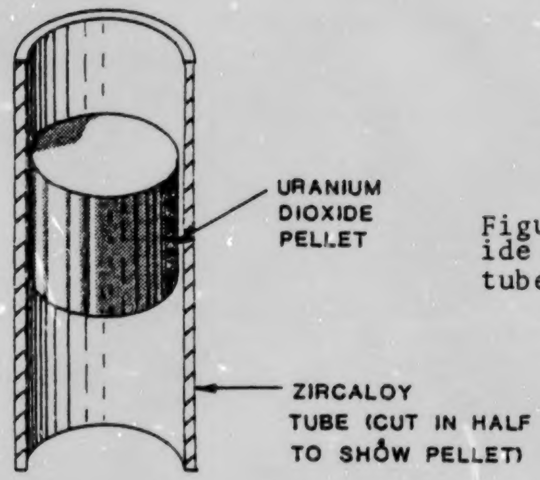

URANIUM DIOXIDE PELLET
ZIRCALOY TUBE (CUT IN HALF TO SHOW PELLET)

Figure 23-1-6. Uranium dioxide pellet enclosed in Zircaloy tube.

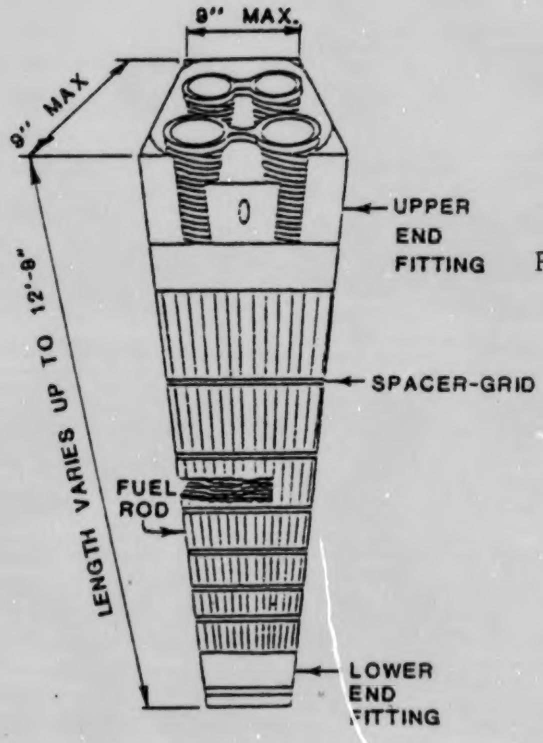

9" MAX.
9" MAX
UPPER END FITTING
SPACER-GRID
FUEL ROD
LENGTH VARIES UP TO 12'-8"
LOWER END FITTING

Figure 23-1-7. Typical PWR fuel assembly.

The BWR fuel assembly also consists of UO_2 pellets in Zircaloy tubing. These rods are assembled into fuel bundles of 64 fuel rods in an 8 x 8 array supported by an upper and a lower tie plate (Figure 23-1-8) approximately 14'-0" apart.

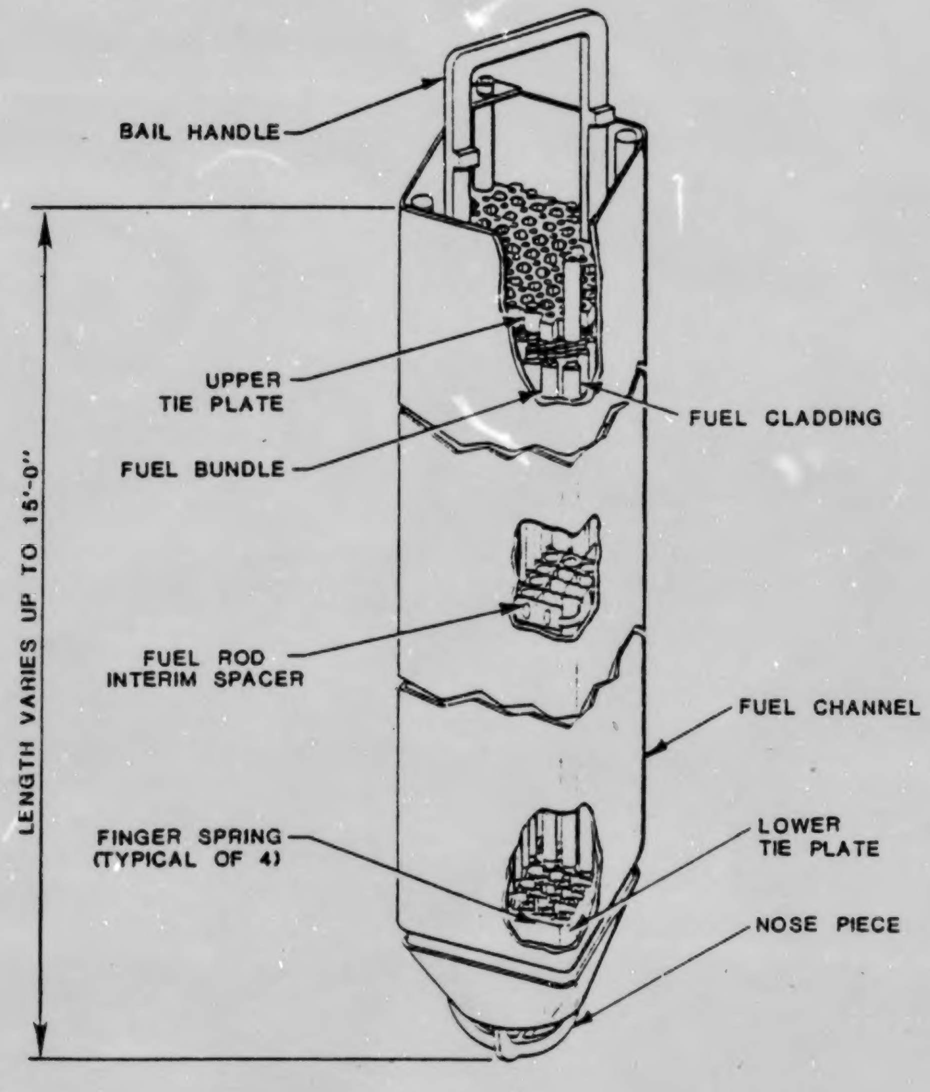

BAIL HANDLE
UPPER TIE PLATE
FUEL CLADDING
FUEL BUNDLE
LENGTH VARIES UP TO 15'-0"
FUEL ROD INTERIM SPACER
FUEL CHANNEL
FINGER SPRING (TYPICAL OF 4)
LOWER TIE PLATE
NOSE PIECE

Figure 23-1-8. Typical BWR fuel assembly.

Quality-control checks are extremely rigid during the entire fabrication process. After fabrication, the fuel is sent to a nuclear power facility to be converted again into energy.

SPENT FUEL PROCESSING

After an assigned period in a reactor and a long period in a spent-fuel pit (while its high-radiation, short-life radionuclides decay), the spent fuel is shipped to a fuel reprocessing plant, at which plutonium and residual uranium can be reclaimed.

Spent fuel usually has been allowed to "cool" for at least one to two years before it is shipped to a reprocessing plant, although the current backlog of spent fuel will mean that it will be aged for at least five years. This cooling allows short-half-life radioisotopes to decay, reducing the levels of penetrating radiation and the heat produced by the assembly. The spent fuel then can be shipped to the reprocessing facility inside shielded shipping casks designed to provide safe and economical means of containing radioactivity. These containers provide (1) adequate shielding against penetrating radiation, (2) criticality control, and (3) containment of materials. Because spent fuel produces both gamma and neutron radiation, spent-fuel casks must be equipped with both gamma and neutron shields. The gamma shield is a dense material such as lead, steel, or depleted uranium. The neutron shield must contain large amounts of hydrogen to be effective; therefore water (to which ethylene glycol has been added to prevent it from freezing) often is placed in a steel jacket immediately outside the gamma shield.

Spent-fuel casks are manufactured in both small and large configurations. Small casks, limited to 25 tons gross weight can be transported by truck. Their payload normally is one spent-fuel assembly from a PWR or two assemblies from a BWR.

Large casks (Figure 23-1-9) weigh up to 100 tons or more and are shipped by rail or barge. They can have a payload of possibly 20 BWR or 10 PWR assemblies. Since the decay heat load of these casks is approximately 50 to 100 KW, a system of forced cooling – frequently by water – is necessary. Large casks are equipped with valves to permit the sampling of the primary coolant; with interchangeable heads and internals to accommodate either PWR or BWR fuel bundles; and with audible alarm systems that activate if the cask temperature exceeds a predetermined value. The stainless steel outer jacket is corrugated for strength and resistance to damage.

The Department of Transportation (DOT) provides mandatory guidelines for the shipment of radioactive materials. These regulations are discussed in detail in "Radiation Protection" Module 21-5, "Regulations for Transporting Radioactive Materials," and in Modules 21-6 and 25-7 (duplicates), "Packaging and Monitoring of Radioactive Materials for Shipment."

Specific areas of the spent-fuel reprocessing plant are designated as receiving-and/or-storage areas. The shipper delivers the cask to these areas.

A receiving-and-storage facility is a large, massive structure of concrete and steel set deep into the ground. All spent fuel to be recovered is handled in this facility. A typical facility contains a deep-water receiving pool for

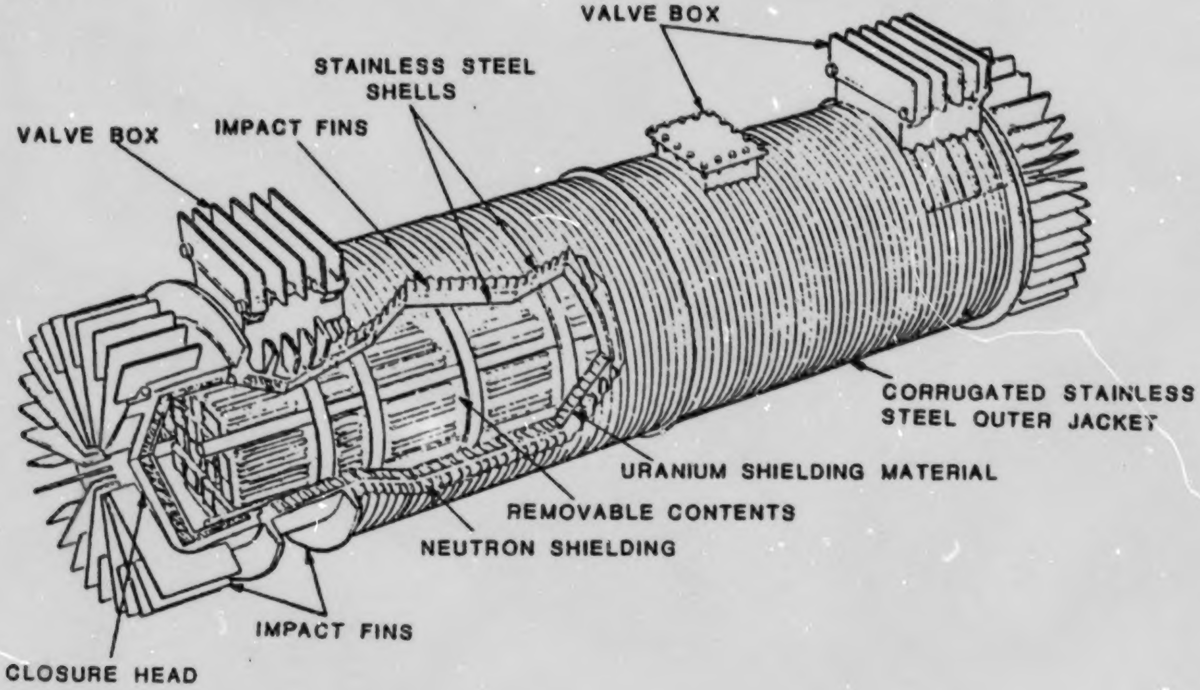

VALVE BOX
STAINLESS STEEL SHELLS
VALVE BOX
IMPACT FINS
CORRUGATED STAINLESS STEEL OUTER JACKET
URANIUM SHIELDING MATERIAL
REMOVABLE CONTENTS
NEUTRON SHIELDING
IMPACT FINS
CLOSURE HEAD

Figure 23-1-9. Fuel shipping cask.

the shipping casks; a shallower, water-filled storage basin, in which the contents of the cask may be stored; a 100-ton-capacity crane, set within a curbed decontamination stall; auxiliary hoists; and a 5-ton fuel-transfer hoist installed on a service bridge that extends across the storage pool (Figure 23-1-10).

Before a cask is placed in the storage pool, it is monitored and thoroughly washed down to remove road grime, especially salts used in snow removal during the winter months.

The fuel is unloaded from the casks under water for both cooling and radiation-shielding purposes. Any special handling, such as encapsulation of broken or cracked fuel assemblies, is performed in the cask unloading pool. The removed fuel is transferred, one assembly at a time, to storage canisters by special tools attached to a fuel-assembly transfer crane. The storage canisters are transferred individually to predetermined locations in the fuel-storage basin, where they are stored in racks in array safe from criticality until the fuel is reprocessed.

For processing, the canisters are taken from storage in a planned sequence and transferred under water by conveyor to an entry port in a mechanical processing cell, where a crane removes the assemblies from the storage canisters. The canisters are returned to the storage pool and replaced in a storage rack for reuse. The unloaded casks are removed from the pool to a cask decontamination area, at which the empty casks are cleaned, monitored, and prepared for return to the reactor site. The shipping cask itself is set within a curbed decontamination stall and is decontaminated by being washed down for the removal of low-activity residual contaminant. The washdown solution is drained into a low-activity waste treatment facility.

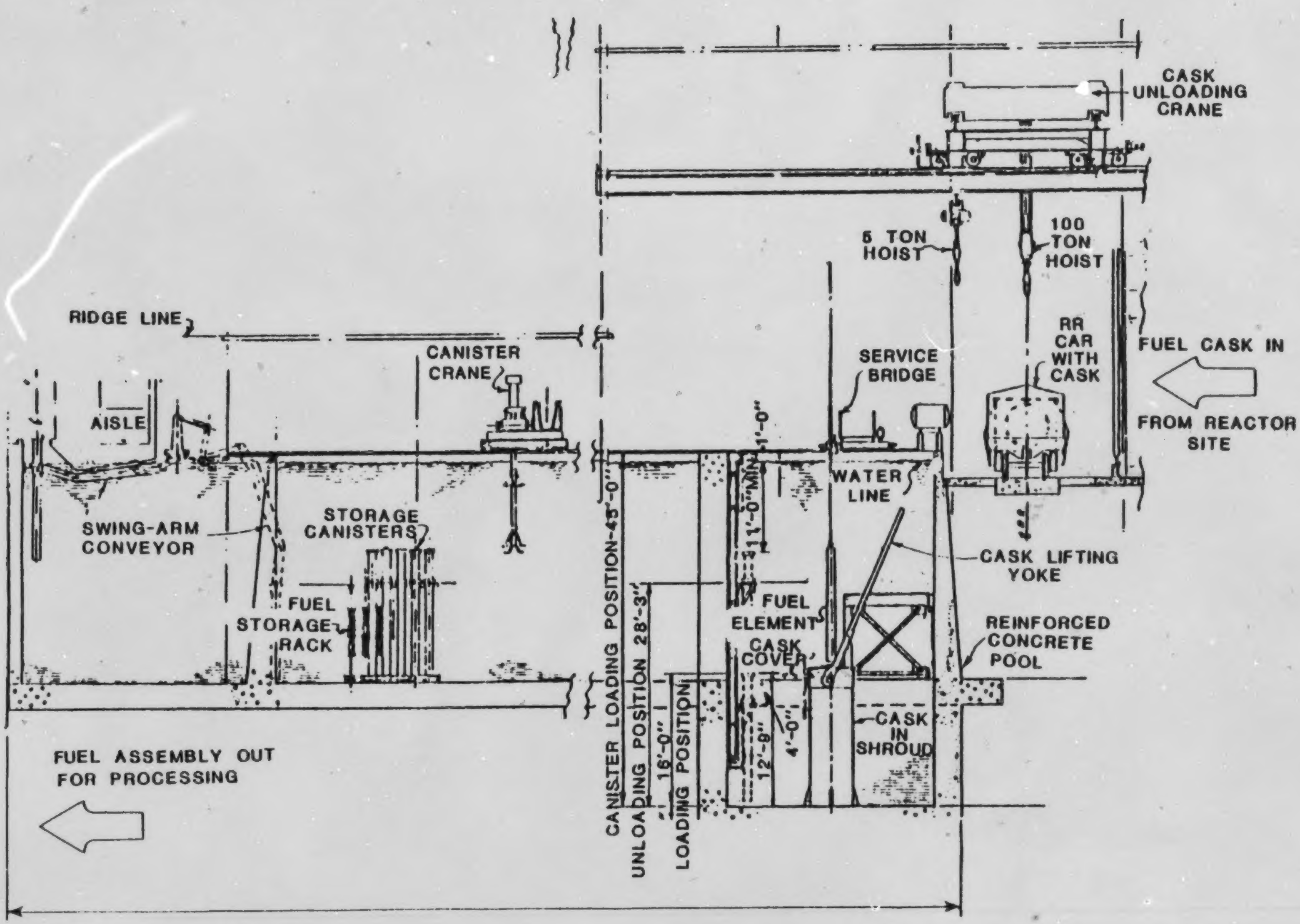

CASK UNLOADING CRANE
5 TON HOIST
100 TON HOIST
RIDGE LINE
CANISTER CRANE
SERVICE BRIDGE
RR CAR WITH CASK
FUEL CASK IN
FROM REACTOR SITE
AISLE
WATER LINE
SWING-ARM CONVEYOR
STORAGE CANISTERS
CASK LIFTING YOKE
FUEL STORAGE RACK
FUEL ELEMENT CASK COVER
REINFORCED CONCRETE POOL
CASK IN SHROUD
11'-0" MIN
1'-0"
12'-9"
4'-0"
CANISTER LOADING POSITION-45'-0"
UNLOADING POSITION 28'-3"
16'-0"
LOADING POSITION
FUEL ASSEMBLY OUT FOR PROCESSING

Figure 23-1-10. Section of fuel receiving, unloading, and storage areas of a commercial reprocessing plant.

MECHANICAL PROCESSING

Since power reactor elements made of Zircaloy are very difficult to dissolve, these elements are mechanically broken (sheared) into short pieces; and the fissile or fertile fuel is leached out, leaving the cladding intact. The shearing force required to break the fuel depends upon the shape of the blade and cross section of the different assemblies and is in the range of 40 to 220 tons of force. The fuel is leached out with nitric acid (HNO_3). The mechanical processing operations of the cropping, the disassembly, and the shearing of power reactor fuel elements into short pieces (1 to 2 inches in length) is practiced in all commercial reprocessing plants. Depending upon assembly, cropping by an abrasive saw requires approximately 2 minutes. A laser can crop them in about 18 seconds.

These operations are carried out in a heavily-shielded and remotely-operated facility that contains air or an inert atmosphere of nitrogen or argon. The facility is located adjacent to the fuel storage basin and is the "mechanical processing cell." Operations carried out in it usually are referred to as "head-end processing" of spent fuel because these steps prepare the fuel for recovery in the downstream PUREX solvent-extraction portion of the plant. Typical mechanical cells and typical steps for head-end fuel reprocessing are illustrated in Figures 23-1-11 and 23-1-12.

A mechanical processing cell may be a rectangular structure whose interior is approximately 14' in width, 50' in length, and 25' in height. For radiation shielding, the walls, which contain viewing windows, are constructed of concrete (4' in thickness of the high-density type or 5 1/2'

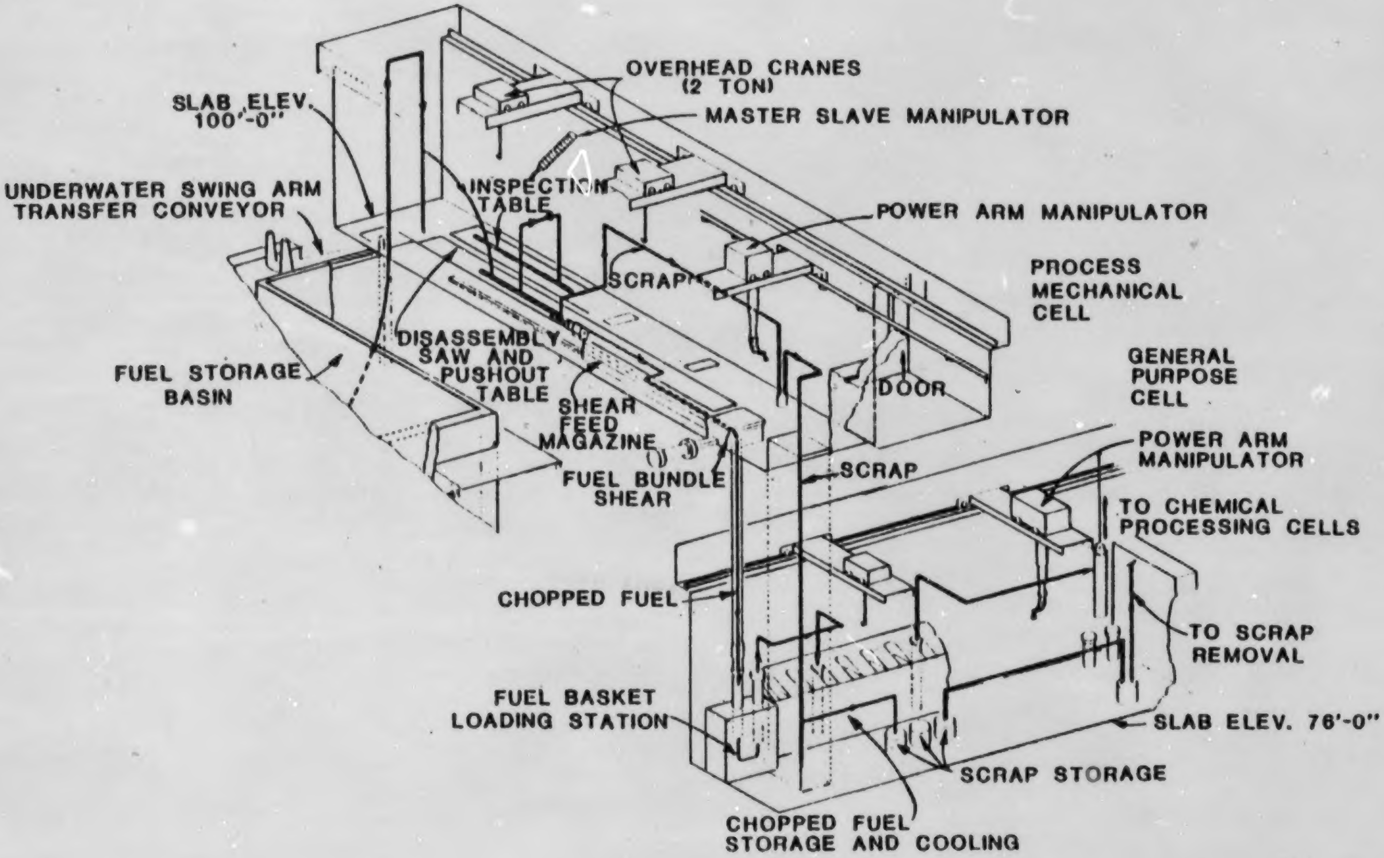

OVERHEAD CRANES
(2 TON)
MASTER SLAVE MANIPULATOR
SLAB ELEV. 100'-0"
UNDERWATER SWING ARM TRANSFER CONVEYOR
INSPECTION TABLE
POWER ARM MANIPULATOR
SCRAP
PROCESS MECHANICAL CELL
DISASSEMBLY SAW AND PUSHOUT TABLE
FUEL STORAGE BASIN
SHEAR FEED MAGAZINE
DOOR
GENERAL PURPOSE CELL
POWER ARM MANIPULATOR
FUEL BUNDLE SHEAR
SCRAP
TO CHEMICAL PROCESSING CELLS
CHOPPED FUEL
TO SCRAP REMOVAL
FUEL BASKET LOADING STATION
SLAB ELEV. 76'-0"
SCRAP STORAGE
CHOPPED FUEL STORAGE AND COOLING

Figure 23-1-11. Arrangement of the head-end mechanical cells and equipment in a commercial reprocessing plant.

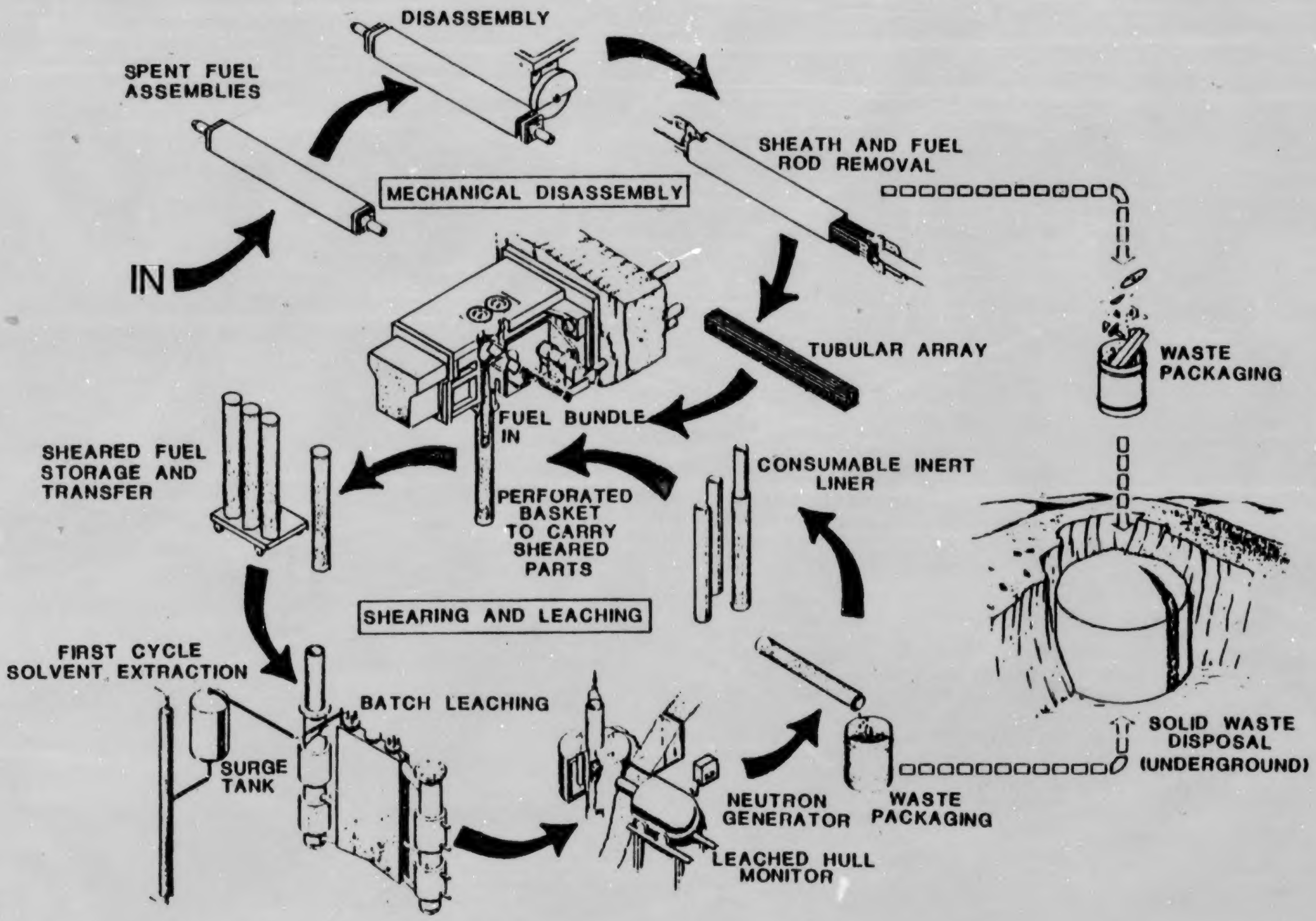

DISASSEMBLY
SPENT FUEL ASSEMBLIES
IN
MECHANICAL DISASSEMBLY
SHEATH AND FUEL ROD REMOVAL
TUBULAR ARRAY
WASTE PACKAGING
FUEL BUNDLE IN
SHEARED FUEL STORAGE AND TRANSFER
PERFORATED BASKET TO CARRY SHEARED PARTS
CONSUMABLE INERT LINER
SHEARING AND LEACHING
FIRST CYCLE SOLVENT EXTRACTION
BATCH LEACHING
SURGE TANK
NEUTRON GENERATOR
WASTE PACKAGING
LEACHED HULL MONITOR
SOLID WASTE DISPOSAL (UNDERGROUND)

Figure 23-1-12. Head-end fuel reprocessing equipment at a commercial plant.

of the ordinary type). The floor and interior walls may be covered with stainless steel to aid in the control of radioactive contamination. Areas of the cell not protected by stainless steel are painted with a light-colored, radiation-resistant protective coating that facilitates viewing and decontamination. Direct viewing is supplemented by TV cameras. The cell interior is illuminated by high-intensity lighting.

Cells are vented in order that a slight negative pressure will be maintained, and all gas discharged from the cell is filtered.

The cell connects to both the fuel storage basin and the chemical processing portion of the plant. The underwater swing-arm transfer conveyor brings the fuel from the fuel storage basin. Two overhead cranes may be used to handle the fuel and convey it to a saw, which "crops" the subassembly (removes the unfueled inlet and outlet coolant nozzles). Fuel rods are withdrawn and fed into a shearing mechanism. The sheared product falls by gravity down a chute, either into baskets or directly into a dissolver.

Chopped fuel is transferred in a basket by a power-arm manipulator to a chemical processing cell. The baskets are placed in dissolver barrels (Figure 23-1-13). (Semicontinuous dissolvers have been proposed and probably will be utilized in the future.)

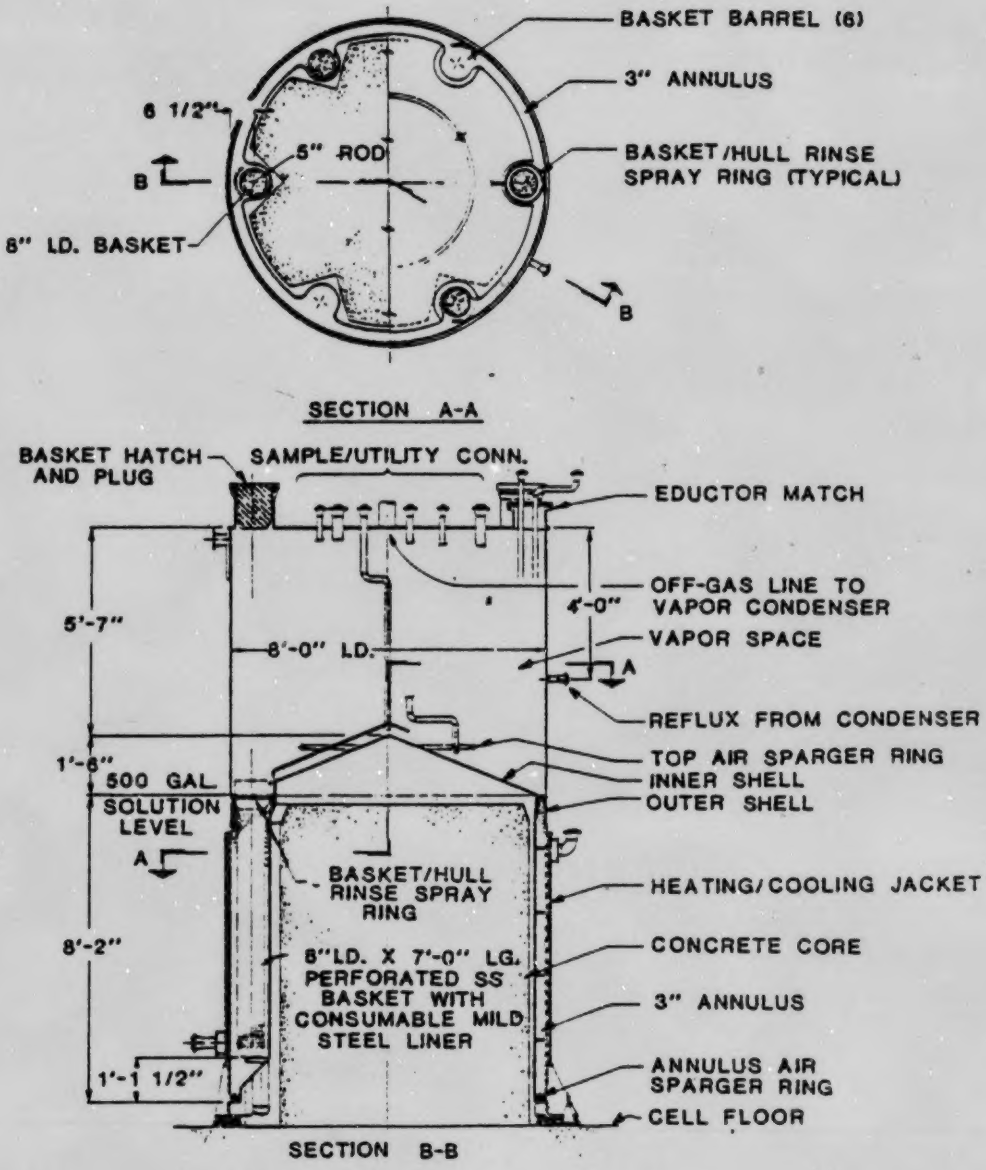

BASKET BARREL (6)
3" ANNULUS
6 1/2"
5" ROD
B
BASKET/HULL RINSE SPRAY RING (TYPICAL)
8" I.D. BASKET
B
SECTION A-A
BASKET HATCH AND PLUG
SAMPLE/UTILITY CONN.
EDUCTOR MATCH
OFF-GAS LINE TO VAPOR CONDENSER
4'-0"
5'-7"
8'-0" I.D.
VAPOR SPACE
A
REFLUX FROM CONDENSER
TOP AIR SPARGER RING
1'-6"
500 GAL. SOLUTION LEVEL
INNER SHELL
OUTER SHELL
A
BASKET/HULL RINSE SPRAY RING
HEATING/COOLING JACKET
8'-2"
8"I.D. X 7'-0" LG. PERFORATED SS BASKET WITH CONSUMABLE MILD STEEL LINER
CONCRETE CORE
3" ANNULUS
1'-1 1/2"
ANNULUS AIR SPARGER RING
CELL FLOOR
SECTION B-B

Figure 23-1-13. Batch dissolver.

The required quantity of acid is metered into the 3" annulus which also fills the barrels. Dissolution reaction begins at about 90°C and subsides after 8 or 9 hours; the solution is boiled 3 or 4 additional hours to insure complete dissolution. Liquid level, specific gravity, temperature, and pressure are monitored throughout the dissolution.

When the dissolution reaction is complete, the solution is cooled and transferred by steam jet to the accountability and feed adjustment tank. Rinse acid is sprayed into the dissolver and jetted to the feed adjustment tank. The baskets containing the hulls are removed from the dissolver, thoroughly rinsed, inspected, sampled, and loaded into 30-gal drums placed in a shielded cask for transport to the burial area. In a 30-gal drum filled with uncompacted hulls, 90% of its volume is air and 10% is Zircaloy metal. Head-end treatment is complete, and processing of the fuel begins.

Accountability Control

During shipping, the shipper retains responsibility for all materials until the authorized receiver officially accepts them.

Before acceptance, the receiver inspects the shipping records, security seals of the truck or railroad car, and seals on each cask. The inspector verifies the cask number, weight, coolant temperature data, and other pertinent information.

When the assemblies are unloaded from the shipping cask, the serial number of each assembly is verified; and the identity, estimated content, and location at which it is to be stored are recorded. All this information is sent to a special plant accountability office whose sole function is to provide accountability for nuclear material. The accountability office then may officially accept the cask.

The accountability form made for a given assembly in the receiving area follows it throughout the facility. Accountability is provided at each step of reprocessing by appropriate sampling devices.

Criticality Control

Criticality control is essential during all phases of spent-fuel shipping and processing since spent fuel is not only highly radioactive but contains significant quantities of fissile material. Control is provided if fuel assemblies are handled in such a manner that a critical arrangement of fuel assemblies cannot be formed.

Under DOT regulations, nuclear spent fuel is classified as a Fissile Class III material and is controlled in transportation by federal regulation and by special arrangements between the shipper and the carrier for nuclear criticality safety.

Spent fuel is removed from the shipping container only after the cask has been placed under water in the unloading basin. It is removed from the cask, either one assembly at a time or as a group of fuel assemblies, and placed in designated positions in the storage rack. The storage racks maintain subcriticality under all normal operating conditions. Protection against criticality is provided by —

- Technical specifications that restrict the fuels that can be received to those whose preirradiation enrichment is less than 5 weight percent ^{235}U.
- Confirmation of fuel type and number of assemblies prior to unloading.
- Critically-safe geometry in the fuel storage canister design.
- Movement of only one fuel canister at a time, in aisles but never over stored fuel.
- Fuel storage racks that guarantee safe geometric spacing, even during earthquakes and tornadoes.

Additionally, criticality control is provided in the mechanical processing cell by limits on the number of fuel assemblies that can be handled in the cell at once; a facility designed in such a manner that it cannot be flooded with a neutron moderator; administrative controls and procedures that must be followed by employees; and geometry control, batch control, and use of neutron absorbers in dissolver acid solution.

Fire Control

Fire control is especially important in a mechanical processing cell. Zircaloy hulls are somewhat pyrophoric (having the tendency to catch fire spontaneously when exposed to air) and pose an inorganic fire hazard. For cells that contain an air atmosphere, CO_2 gas systems can extinguish organic fires; and foam or sand can extinguish inorganic fires.

Chemical Processing

After the fuel is dissolved away from the cladding with nitric acid, an organic solvent extracts plutonium and uranium; and additional solvent extraction operations separate the two substances. Plutonium is converted to plutonium oxide (PuO_2); ^{235}U, to UO_2. These products then can be combined to make a mixed oxide fuel and can be formed into replacement fuel rods and assemblies for use in nuclear reactors. These processes are explained in the modules that follow.

EXERCISES

1. Outline the generalized nuclear fuel cycle (when operating) of the United States.
2. What are the major head-end reprocessing steps?
3. How does the head-end interface with the downstream solvent extraction process?
4. What nuclear criticality safety procedures are followed in the head-end process?

MATERIALS

Shear-Leach Process for Spent Nuclear Fuels
Film Number 0339
Print Number: 011

DOE TIC Film Library
P.O. Box 62
Oak Ridge, TN 37830

PROCEDURES

View the film "Shear-Leach Process for Spent Nuclear Fuels." Answer the following questions.

1. Why was the mechanical shear-leach process first developed?

2. Why is the equipment utilized in the shearing process fabricated steel that is resistant to nitric acid?

3. How is the end hardware of a nuclear fuel assembly removed?

4. How are sheared pieces and fines contained after shearing?

5. What precautions are taken to prevent contamination by fines?

6. What happens to the empty clad material after dissolution?

7. What 3 types of cutting methods separate the head-end hardware of a nuclear fuel assembly?

8. About what percentage of the core assembly is crushed as fines?

9. How much time is required to leach out unirradiated uranium?

10. What effect does irradiation have on leaching time?

DATA TABLE

None.

44

REFERENCE MATERIALS

A Guide to the Selection, Training and Licensing or Certification of Reprocessing Plant Operators, Volume II. Oak Ridge, TN: Oak Ridge National Laboratory, 1976.

"Chemical Processing of Irradiated Fuels, TID-7583." Richland, WA: United States Atomic Energy Commission, Technical Information Service, 1959.

Lish, Kenneth C. *Nuclear Power Plant Systems and Equipment*. New York: Industrial Press, 1972.

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U.S. Department of Energy. *Barnwell Nuclear Fuels Plant Applicability Study*. Volume 2, *BNFP-Utilization, Evaluations and Conclusions*. Springfield, VA: National Technical Information Service (NTIS), U.S. Department of Commerce, April, 1978.

Film:

Shear-Leach Process for Spent Nuclear Fuels
Film Number 0339
DOE TIC Film Library
Oak Ridge, TN 37830

PART I – MULTIPLE CHOICE

Choose the best response(s) to the following questions by circling the choice.

1. The chief difference between the PWR and BWR reactor is –
   a. The reactor coolant in the BWR is ordinary water.
   b. The PWR is cooled by water under pressure, the BWR is not cooled by water.
   c. Boiling water in the BWR boils in pipes that travel through the reactor core, coolant water in the PWR passes directly through the reactor core.
   d. The PWR is cooled by pressurized water in the reactor; coolant water in the BWR boils to steam inside the reactor.

2. The correct sequence of the basic steps of yellowcake and UO_2 production is –
   a. Mining, milling, conversion to UF_6, purification of UF_6 to UO_2, and enrichment.
   b. Mining, milling, leaching, enrichment, conversion to UF_6, conversion to UO_2.
   c. Mining, milling, gaseous diffusion, conversion to UF_4, conversion to crude UF_6, UF_6 purification, enrichment, conversion to UO_2.
   d. Mining, milling, leaching, production of yellowcake, chemical production of UO_2, conversion to UF_4, conversion to crude UF_6, UF_6 purification, enrichment, and conversion to UO_2.

3. Gaseous diffusion works because –
   a. Lighter molecules diffuse faster than heavier molecules because of their greater velocity.
   b. Heavier molecules cannot pass through barriers in the diffusion cascades.
   c. The molecules of uranium $^{235}UF_6$ travel faster than the molecules of uranium $^{238}UF_6$.
   d. The molecules of uranium $^{238}UF_6$ travel faster than the molecules of uranium $^{235}UF_6$.

4. The gas introduced into the Zircaloy tubes of the fuel assembly –
   a. Argon.
   b. Helium.
   c. Hydrogen.
   d. Krypton.

5. Large spent-fuel shipping casks may carry a payload of –
   a. No more than 10 BWR assemblies.
   b. No more than 5 BWR assemblies.
   c. 20 BWR or 10 PWR assemblies.
   d. 15 PWR or 5 BWR assemblies.

6. Spent fuel must –
   a. Be shielded only against neutron radiation.
   b. Be shielded only against gamma radiation.
   c. Be shielded against both gamma and neutron radiation.
   d. Be shipped in a critically-safe array.

7. Serial numbers are placed –
   a. On fuel casks only.
   b. On each fuel assembly.
   c. On each fuel rod.
   d. On casks, assemblies, and rods.

8. The preirradiation enrichment of a fuel received at a spent fuel reprocessing plant –
   a. May not exceed 10 weight percent ^{235}U.
   b. May be between 15 and 5 weight percent ^{235}U.
   c. Must be less than 5 weight percent ^{235}U.
   d. Must be less than 2 weight percent ^{235}U.

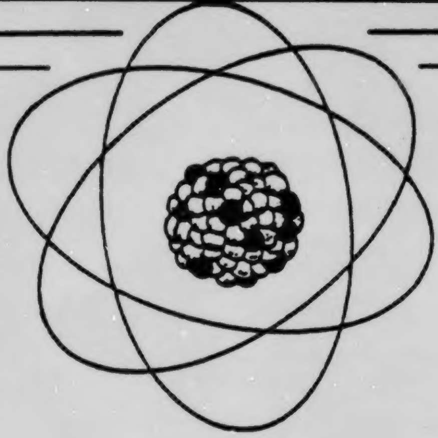
9. Encapsulation of cracked fuel assemblies –
   a. Is performed in the cask unloading pool.
   b. Is performed in the fuel storage basin.
   c. Is unnecessary.
   d. Is performed in the mechanical processing cell.

PART II – ESSAY

10. Describe a typical spent-fuel receiving and storage facility. Include diagrams as necessary.

11. Draw a flow chart of typical major head-end reprocessing steps.

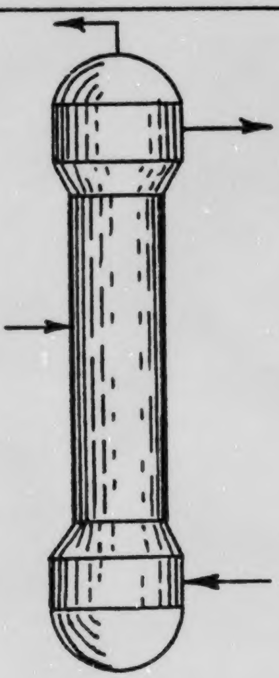
12. Using Figures 23-1-10 and 23-1-11, describe the steps followed in the preparation of a fuel assembly for reprocessing. Include a description of the interface with the downstream solvent extraction process.



NUCLEAR TECHNOLOGY

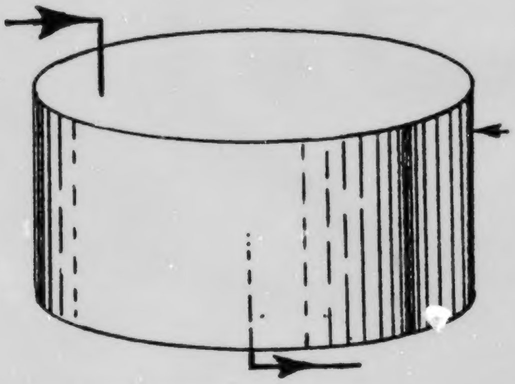
MODULE 23-2

ION EXCHANGE



NUCLEAR CHEMICAL
PROCESSES

COURSE 23



CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

Evaporation and ion exchange are methods of separation and concentration of solutions. Both are used in fuel processing operations.

Ion exchange is the reversible interchange of ions between a liquid phase and a solid material and does not involve a substantial change in the structure of the solid. It occurs when a solid that contains fixed ions and oppositely charged mobile ions is brought in contact with an electrolytic solution. It is one of the most efficient methods of chemical separation and is of special importance in the separation of radioelements. Within the nuclear fuel industry, its most important application is as an auxiliary step with other types of separation processes in the concentration of solutions of Pu, ^{235}U, and ^{233}U.

Evaporation is the volatilization of a solvent or other substance by application of heat and condensation of the subsequent vapor to the liquid state. It offers a high degree of separation between volatile and nonvolatile components of solutions, especially of solutions that are difficult or inconvenient to separate by low-temperature separation operations such as precipitation, filtration, or ion exchange. It is an important part of the PUREX process and is especially important to the concentration of waste solutions.

This module discusses ion exchange and evaporation operations in detail, with special attention to their application in spent-fuel reprocessing.

MODULE PREREQUISITES

The student should have completed courses in basic algebra and chemistry and Module 23-1, "Head-End Treatment."

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    Ion exchange.
    Sorption.
    Ion-exchange resin.
    Cation-exchange resin.
    Anion-exchange resin.
    Ion-exchange capacity.
    Evaporation.
    Demister device.
2. Write equations that describe a typical anion- and a typical cation-exchange reaction.
3. Describe purification of plutonium by anion exchange, detailing the feed absorption, decontamination wash, and product removal steps by constructing a flow chart for each.
4. Describe recover of plutonium by cation exchange.
5. Describe production and composition of anion- and cation-exchange resins.
6. Describe the effect of cross-linking of polymer chains or the rigidity and solubility of the polymer.
7. List factors that may cause the degradation of ion-exchange resin.

8. Describe ion-exchange equipment including –
    - Operation of typical column.
    - Provisions for criticality and radiation safety.
    - A general description of the Higgins quasi-continuous contactor.
9. List streams evaporated in the PUREX process; describe the evaporation process.
10. Sketch and describe the operation of a typical evaporator.
11. List operating procedures for intermittent, semi-continuous, and continuous evaporator operation.

OVERVIEW OF ION EXCHANGE

Ion exchange is a special type of sorption process and is the preferred process for purifying and concentrating fissionable materials from aqueous solutions prior to their conversion into metals. In nuclear fuel processing operations, ion exchange usually follows solvent extraction and provides the final separation of fissionable materials from fission products or other fissionable materials.

Sorption is any process by which one substance takes up and holds the molecules of another substance. In the ion-exchange process, specific ions in an aqueous phase exchange with the ions of an ion-exchange resin phase when the solution comes in contact with the resin. These resins are made of special types of giant molecules that form a polymerized, high-molecular-weight, insoluble electrolyte that has large, heavy ions and oppositely charged small, simple ions that can be exchanged for ions in contact with the resin. These resins are classified as either cation- or anion-exchange resins, depending upon their mode of action. A cation is a positively charged ion, and an anion is a negatively charged ion.

Cation-exchange resins contain small cations, which can be exchanged, and high-molecular-weight anions. Resins of this type, which exchange their cations for cations in the solution, include sulfuric acid derivatives, carboxylic acid derivatives, and silicates. Equation 23-2-1 depicts a typical cation-exchange reaction, with the result of contacting a cation-exchange resin with a solution of sodium chloride.

$$\text{Resin}^{-}\text{-H}^{+} + \text{Na}^{+} + \text{Cl}^{-} \longrightarrow \text{Resin}^{-} - \text{Na}^{+} + \text{HCl}$$

Equation 23-2-1
(Equation = Eq.)

Anion-exchange resins consist of simple anions that can be exchanged for anions in the solution and cations of high molecular weight. They include certain ammonium and polyamine compounds. Equation 23-2-2 describes a typical anion-exchange reaction.

$$\text{Resin}^{+} - \text{OH}^{-} + \text{Na}^{+} + \text{Cl}^{-} \longrightarrow \text{Resin}^{+}\text{-Cl}^{-} + \text{NaOH}$$

Eq. 23-2-2

Anionic resins are subdivided into strong- and weak-based resins; cationic resins, into strong- and weak-acid resins.

Ion-exchange operations usually take place inside vertical columns. As the aqueous solution is pumped through the ion-exchange resin, which is supported in the columns, the ions in the aqueous phase are exchanged with the ions of the resin. The ions on the resin then are eluted (washed off the resin) when it is contacted with a specially prepared eluant. The eluant used with a cationic resin is a strong acid or a cation-complexing agent. Eluants employed with anionic resins are strong bases or complexing agent. After elution, the resin may require reconditioning to return it to the proper state for sorption of the next batch of material.

Within the fuel processing industry, the chief use of ion-exchange operations is the concentration of fissile material and the removal of fission products or fertile material from solution. It is a very effective method because (1) it is not likely to introduce impurities into a solution, and (2) it frequently achieves significant additional purification of the solution while concentrating the fissile material. The purification frequently is enough to eliminate a complete solvent extraction step. Concentration factors in excess of 100 have been demonstrated with simple exchange operations that involve heavy element containing solutions. These same operations often achieve very high decontamination of fission products.

CONCENTRATION OF PLUTONIUM BY ION EXCHANGE

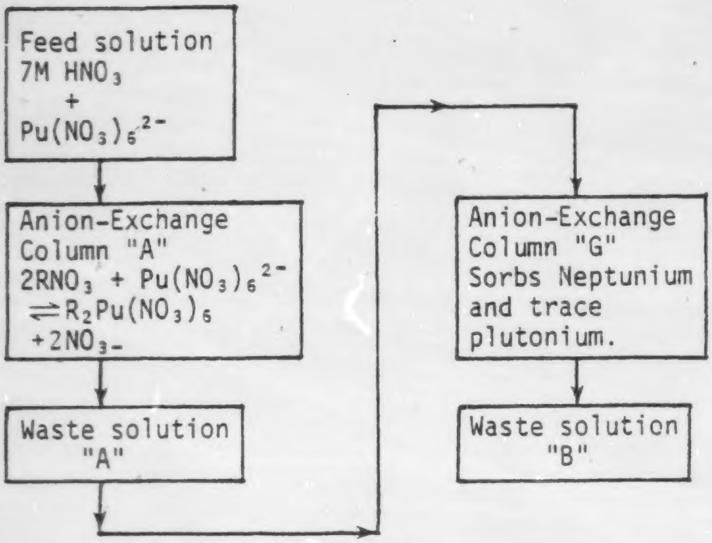
Extremely dilute solutions containing plutonium ions may be concentrated by use of either anion or cation exchange processes.

Concentration of Pu by Anion Exchange

A typical application of ion exchange in the nuclear process industry is the recovery of plutonium from the waste product stream of the PUREX process. The feed solution is acidified with 7 M (molar) HNO_3 in order to convert plutonium cations into the anionic form, $Pu(NO_3)_6^{2-}$. The uranium and neptunium ions which remain as cations in the PUREX waste solution after acidification, are weakly sorbed by the anion exchange resin used to concentrate the anionic form of the plutonium ions. The following exchange occurs during the sorption of $Pu(NO_3)_6^{2-}$ ions on an anion resin (RNO_3):

$$2\ RNO_3 + Pu(NO_3)_6^{2-} \rightleftharpoons R_2Pu(NO_3)_6 + 2\ NO_3^- \qquad \text{Eq. 23-2-3}$$

Plutonium is sorbed by the anion resin (Figure 23-2-1). Waste solution leaving the anion-exchange column contains uranium, neptunium, and a trace of plutonium. The valence of neptunium is adjusted in order to convert it to a cation. Valence is adjusted by contact of the neptunium with a solution of ferrous nitrate and hydrazene in 7M nitric acid. This adjusted feed is passed through an anion-exchange column. The anion resin sorbs the neptunium and trace plutonium. The uranium passes out of the column as a cation. Figure 23-2-1 illustrates these steps, sometimes called the "feed adsorption process."


Feed solution
7M HNO_3
+
$Pu(NO_3)_6^{2-}$
Anion-Exchange Column "A"
$2RNO_3 + Pu(NO_3)_6^{2-} \rightleftharpoons R_2Pu(NO_3)_6 + 2NO_3^-$
Waste solution "A"
Anion-Exchange Column "G"
Sorbs Neptunium and trace plutonium.
Waste solution "B"

"A" WASTE SOLUTION

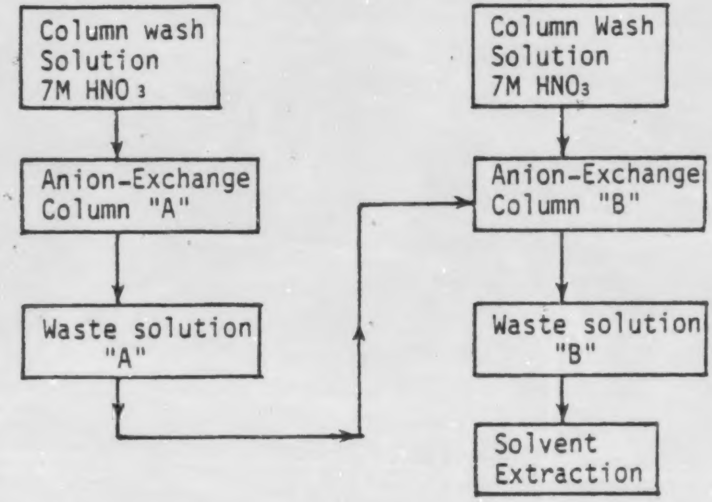
Uranium, Neptunium and trace of Plutonium contacted with ferrous nitrate and hydrazine in 7M nitric acid

"B" WASTE SOLUTION

Uranium as cation, corrosion products and salting agents

Figure 23-2-1. Feed adsorption step.

After the resin in the first column is loaded with plutonium, it is scrubbed with 7M nitric acid to remove neptunium, uranium, fission products, corrosion products, and salting agents. Plutonium is not desorbed from the resin. The resin loaded by neptunium and trace plutonium in the second anion-exchange column also is scrubbed with 7M nitric acid. The neptunium and plutonium remain sorbed on the resin. The final waste products are transferred to the solvent extraction system for purification and for removal of the cationic uranium. Figure 23-2-2 illustrates these steps.


Column wash Solution 7M HNO3
Anion-Exchange Column "A"
Waste solution "A"
Column Wash Solution 7M HNO3
Anion-Exchange Column "B"
Waste solution "B"
Solvent Extraction

"A" WASTE SOLUTION
Uranium, Neptunium, corrosion products, salting agents contacted with ferrous sulfate and hydrazine

"B" WASTE SOLUTION
Uranium, corrosion products, and salting agents

Figure 23-2-2. Decontamination wash step.

After the columns are scrubbed, plutonium and neptunium can be eluted as illustrated in Figure 23-2-3. Plutonium sorbed on the anion-exchange resin is desorbed by passing 0.5M nitric acid through the column. This dilute acid converts plutonium to a cation. The anionic resin containing neptunium also is contacted with the acid and the same reaction occurs. Elution can be performed with any concentration of nitric acid between 0.35 and 0.75 molar. Lower nitric acid concentrations are avoided to prevent the hydrolysis of plutonium.

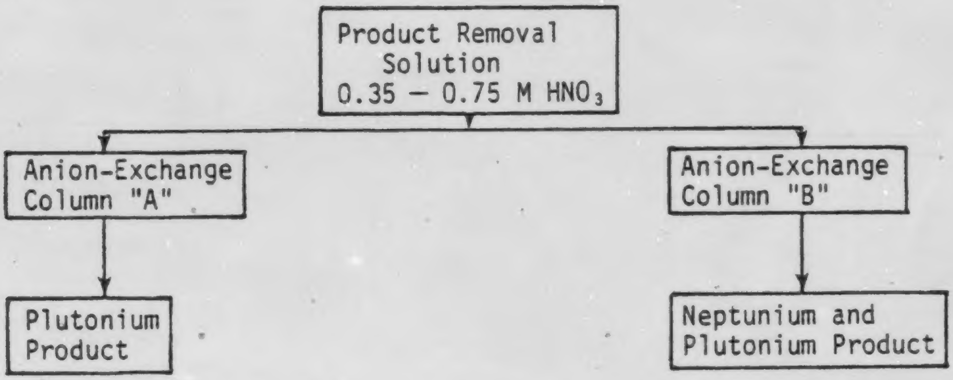

Product Removal Solution 0.35 – 0.75 M HNO_3
Anion-Exchange Column "A"
Anion-Exchange Column "B"
Plutonium Product
Neptunium and Plutonium Product

Figure 23-2-3. Product removal step.

Concentration of Pu by Cation Exchange

Plutonium also can be recovered by cation exchange. The feed consists of Pu^{3+} complex at a low (0.25 molar) nitric acid concentration with an hydroxylamine complexing agent at a concentration of 0.025 molar. A sulfonic acid cation-exchange resin is used. The following reaction occurs when the feed contacts the resin:

$$3HR + Pu^{3+} \rightleftharpoons PuR_3 + 3\,H^+ \qquad \text{Eq. 23-2-4}$$

The cation-exchange resin containing sorbed plutonium is scrubbed with 0.24 M sulfuric acid to remove uranium, zirconium, and niobium. Residual metal sulfate salts are scrubbed from the column with demineralized water. Plutonium sorbed on cation-exchange resin is eluted from the resin by a strong nitric acid that contains sulfonic acid. The sulfonic acid prevents occurrence of gases that would result if Pu^{3+} were oxidized by nitric acid.

Use of the cation-exchange resin to recover plutonium requires that the resin be reconditioned prior to the next sorption step by being washed with dilute nitric acid that contains hydroxylamine sulfate. This process returns the resin to the proper state of sorption for the next batch of material.

Cation-exchange resins rapidly sorb uranium from a dilute uranyl nitrate solution. Uranium then can be eluted at 50 to 60 grams per liter by 6 M nitric acid. Up to 250 grams per liter can be achieved by elution of the uranium with a combination ammonium citrate and ammonium acetate solution.

ION-EXCHANGE RESINS

Ion-exchange resins are polymerized, cross-linked hydrocarbons that contain ionizable groups. They are, in essence, three-dimensional matrices of hydrocarbon chains with ion-exchange sites distributed throughout the entire resin particle. These ion-exchange sites contain ionic units attached to the polymer chains and have an affinity for either negative (anionic) or positive (cationic) particles. Anionic exchangers are produced by the introduction of bases (simple or complex amine groups) into the resin structure. The introduction of acidic groups produces cation exchangers. Sulfonic groups produce strong-acid cation resins. Carboxylic groups produce weak-acid cationic resins.

Resins consist of polystyrene copolymerized with divinylbenzene to build up the three-dimensional cross-linked chain. The ion-exchange sites protrude from these polymer chains. Figure 23-2-4 depicts a typical cross-linked polystyrene.

Cross-linking of the chains increases rigidity of the polymer, decreases its solubility, and reduces swelling and shrinkage that occur during the sorption-desorption cycle. Because of the strenght of the carbon-carbon bond of the hydrocarbon, the resins are exceptionally stable, although the chemical stability of anion exchangers is much less than that of the cation exchanger because of the relatively low strength of the carbon-nitrogen amine linkage present in these resins. Table 23-2-1 lists some commercially available ion-exchange resins and their properties. Dowex 50 is the most popular cation-exchange resin in the ion-exchange plutonium-separation process.

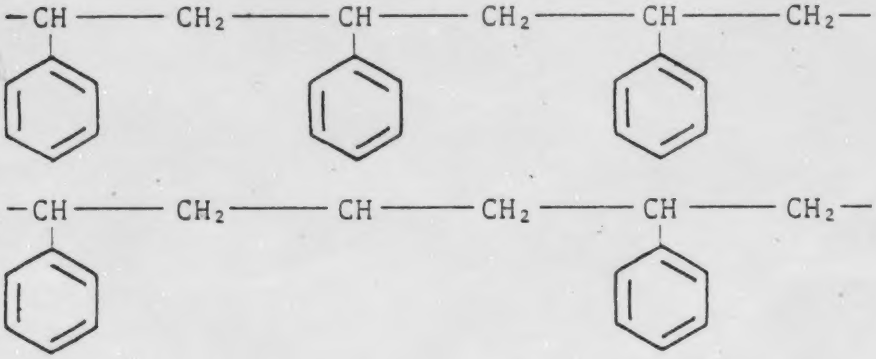


Figure 23-2-4. Cross-linked polystyrene.

One important characteristic listed on Table 23-2-1 is each resin's ion-exchange capacity; the measure of its ability to take up counter ions in a unit volume or weight of a resin. The capacity depends upon the ionic form of the resin, although actual operating capacity of a resin usually is lower than theoretical capacity.

All types of resins degrade when irradiated. Table 23-2-2 lists radiation stability of some resins.

Usually, bonds on long hydrocarbon chains can be broken down by cumulative doses of radiation in the 6×10^{10} rem range. Tests also have shown that irradiation of 1.7×10^{9} rem results in 25% of total cation-exchange capacity being lost. Because of this degradation, records of exposure of resin to radioactivity are kept; and the resin column or the resin itself is changed prior to degradation.

Resins are exposed to high concentrations of nitric acid for as short a time as possible. High concentrations of this acid, especially at temperatures abouve 70°C, can nitrate the resin and cause severe damage. Explosions are possible.

Dry resins deteriorate rapidly, and resins always are stored underwater.

TABLE 23-2-1. COMMERCIAL ION-EXCHANGE RESINS.

Name	Type	Effective operating pH range	Functional group	Ionic form	Exchange capacity	
					dry resin (mEq/g)	wet resin (mEq/ml)
Dowex 50	Strongly acidic cation exchanger	0-14	$-SO_3^-H^+$; polystyrene	H or Na	4.3	1.9
Amberlite IR-120		0-14			4.2	1.9
Duolite C-20					5.1	2.1
Wofatit KPS		0-12			4.5	1.3
Zeokarb 225					5.0	2.4
Amberlite IRA-400	Strongly acidic anion exchanger	0-14	Quaternary amine	Cl	3.3	1.2
Dowex 1		0-14	$-CH_2-\overset{+}{N}(CH_3)_3$; polystyrene		3.3	1.2
Duolite A-101		0-14			4.0	1.3
Deacidite FF		0-12			3.5	1.5
Amberlite IRA-410		0-12	$-CH_2-\overset{+}{N}(CH_3)_2C_2H_4OH$		3.1	1.35
Dowex 2		0-14			3.3	1.2
Amberlite IR-4B	Weakly or medium basic	0-7	-NHR or $-NR_2$; phenol or polyamine condensation	OH	10	2.5
Wofatit MD					5.7	2.0
Amberlite IR 45		0-7	Polystyrene; -NHR or $-NR_2$		5.0	2.0
Dowex 3		0-7			5.5	2.5
Amberlite IRC 50	Weakly acidic	7-14	Polyacrylic or polymethacrylic acid	H	10	3.5
Duolite CS 101					10.2	3.3
Duolite ES 63	Medium acidic		Polystyrene $-PO(OH)_2$		6.6	3.1
Duolite C 3	Strongly acidic		Phenol condensation; $-SO_3^-H^+$		2.9	1.2

TABLE 23-2-2. RADIATION STABILITY OF ION-EXCHANGE RESINS.

	Capacity change, %				Moisture change, %			
Resin	1×10^7 r	2×10^8 r	3.8×10^8 r	1.7×10^9 r	1×10^7 r	2×10^8 r	3.8×10^8 r	1.7×10^9 r
Sulfonic Polystyrene								
Dowex-50	0		-15, -9	-23				
Dowex-50W		-5.4	-8.7	-98±				
Nalcite HCR			-8					
Amberlite IR-120	0,0		-9		+3, +2	+20, +10		
Amberlite IR-112 (porous)	0		+7		+16, +6	+20, +10		
Permutit Q			-2					
Carboxylic Sulfonic Polystyrene								
Amberlite XE-111	0	-7			+2, +1	+20, +10		
Amberlite C-1		-7	-10, -23			+4	+7	+17
Nepton CR-61		-7	-11,-27			-2	-20	- 1.5
Sulfonic Phenolic								
Amberlite IR-105	0		-1					
Amberlite IR-100		-15			-3, -10	-7, -8		
Dowex-30			-1					
Nepton CR-51		-3	-1, -6	-28		+1, -13	+2, -12	-4, +13
Strongly Basic								
Amberlite IRA-400	0.2	-45,-30	-42		+7, -8	-18, -18		
Amberlite IRA-401 (porous)	0	50, 27			+1, -1	- 6, 15		
Amberlite IRA-410	4	-35,-20	-40		+7, +16	- 2, -2		
Amberlite IRA-411 (porous)	9	-50,-38			+4,-4	-21, 32		

ION-EXCHANGE EQUIPMENT

Ion-exchange columns are cylindrical, vertical columns filled with sorbing granules of ion-exchange resin. Feed solution is pumped through the column and collected in a product storage tank. Elutriant also is pumped through the column and collected in a solution storage tank from which it is returned to a solvent extraction system for recovery of fissile materials. Diameter of the columns is six inches or less to provide a critically safe geometry. The resin usually is contained by screens. Normally, two resin columns are operated in parallel in order that one may be eluted while the other is being loaded. Columns are located in an accessible area, since the solutions conducted through them have been effectively decontaminated by solvent extraction. Such accessiblity aids in the removal of the column or the resin after the end of its life. There is a danger, however, that after several cycles, trace quantities of fission products may accumulate on the resin. These products must be removed if shielding is not employed. In concentration of plutonium, fission products are washed from the resin with oxalic acid.

One ion-exchange system in general use is the Higgins quasi-continuous contactor illustrated in Figure 23-2-5. In this system, four different operating sections — loading and scrubbing, resin storage, resin actuation, and elution — are connected by means of control valves. When the black valves are closed and the white valves are open, the operation proceeds as follows:

- Feed passes through the resin in the loading section: Plutonium is sorbed. Neptunium, uranium, and other impurities leave in the waste stream. When the resin

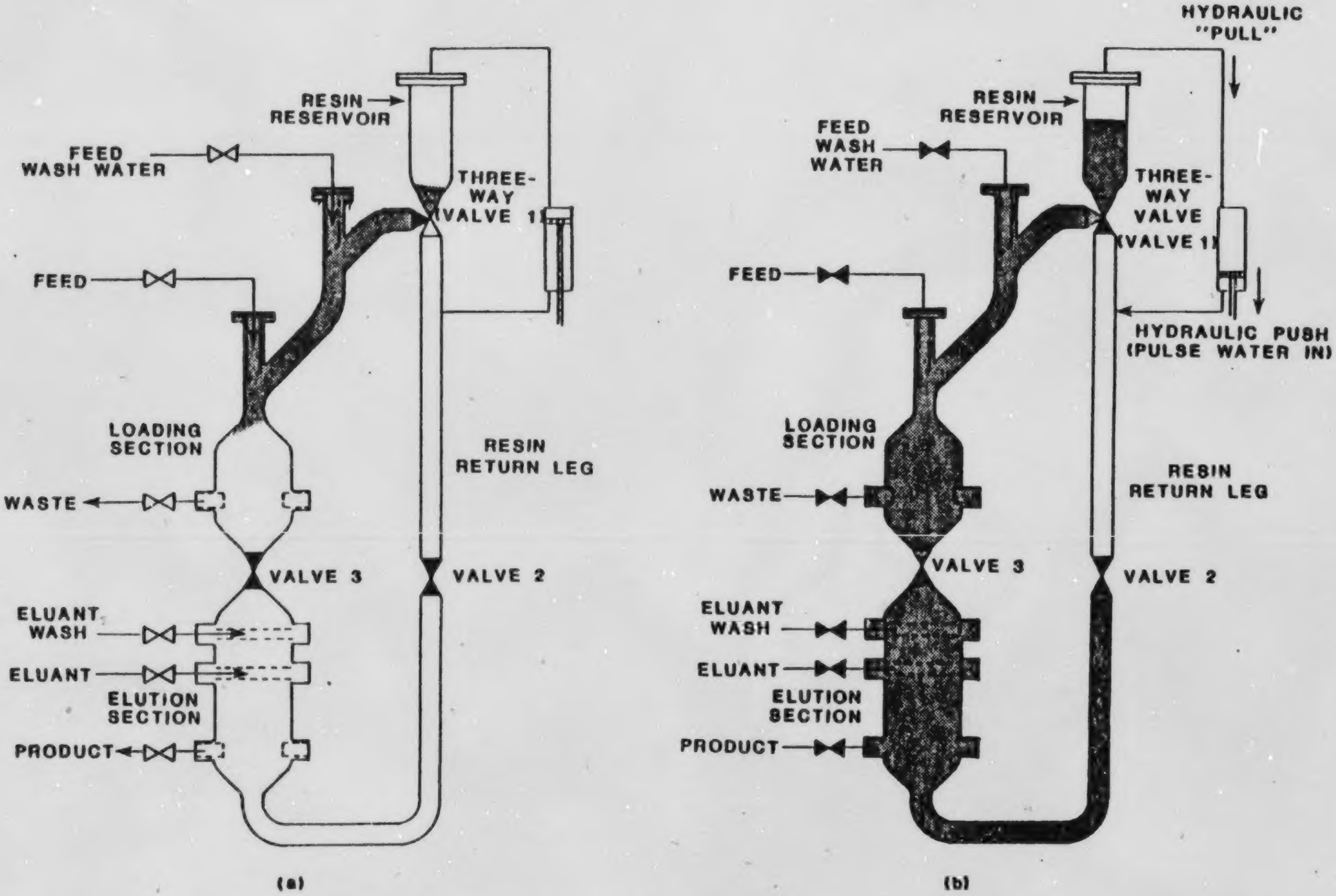

RESIN RESERVOIR
FEED WASH WATER
THREE-WAY VALVE 1
FEED
LOADING SECTION
RESIN RETURN LEG
WASTE
VALVE 3
VALVE 2
ELUANT WASH
ELUANT
ELUTION SECTION
PRODUCT
(a)
HYDRAULIC "PULL"
RESIN RESERVOIR
FEED WASH WATER
THREE-WAY VALVE (VALVE 1)
FEED
HYDRAULIC PUSH (PULSE WATER IN)
LOADING SECTION
RESIN RETURN LEG
WASTE
VALVE 3
VALVE 2
ELUANT WASH
ELUANT
ELUTION SECTION
PRODUCT
(b)

Figure 23-2-5. Mode of operation of a Higgins quasi-continuous ion-exchange contactor. (a) During pulse period. (b) During sorption period.

is saturated with plutonium, feed flow is stopped; and a scrubbing solution is passed through the resin (Figure 23-2-5a).

- Resin in the lower vessel already is loaded with plutonium. (Notice that valves connected to the vessel are closed.) This plutonium was sorbed in a previous cycle. At the same time plutonium is being sorbed and the resin washed in the upper vessel, plutonium in the lower vessel is converted to the cation form that causes it to leave the unit in the product stream. Some loaded resin from the resin reservoir drains through the open section of the three-way valve 1 into the resin-return leg above valve 2 (Figure 23-2-5a).
- When these operations are completed, valves are set as in Figure 23-2-5b. During this pulse period, push water forces loaded resin counterclockwise from the resin-return leg into the elution section, eluted resin into the loading section, and loaded resin into the resin reservior through the open section of three-way valve 1 (Figure 23-2-5b).

EVAPORATION

Evaporation is a means of concentrating a solution by boiling away the solvent from the solutes. In fuel reprocessing it is used to reduce volume of liquid waste and product solutions; to reduce amount of radioactive material in liquid effluents; to recover nitric acid for reuse; and to reduce concentration of acidic waste, thereby reducing the amount of caustic soda (NaOH) needed to neutralize the waste. In the PUREX process, evaporated streams are –

- High-activity waste from the first solvent cycle.
- Intercycle uranium stream.
- Second cycle waste.
- Product uranium and plutonium streams.

EQUIPMENT

Evaporators include devices that transfer heat for boiling the solution, that separate vapor phase from liquid phase, and that condense the vapor to a liquid. Figure 23-2-6 and 23-2-7 illustrate two commonly used types of evaporators.

Steam is the heat source and is supplied to a jacket around the lower part of the pot or to internal coils of pipe or bundles of tubes. The feed circulates around these tubes or pipes where it boils, the vapor rising to the disengaging section of the evaporator. In Figure 23-2-6 and 23-2-7 this stage is referred to as a demister device. This device may contain baffles to make the vapor change direction, causing the liquid droplets entrained in the vapor to fall out of the stream, or it may contain wire mesh on which the droplets collect before draining down the vessel walls. After passing through the demister, the vapor passes through a bubble-cap column that removes any traces of entrained liquid and passes into a water-cooled condenser that converts the vapor to a liquid.

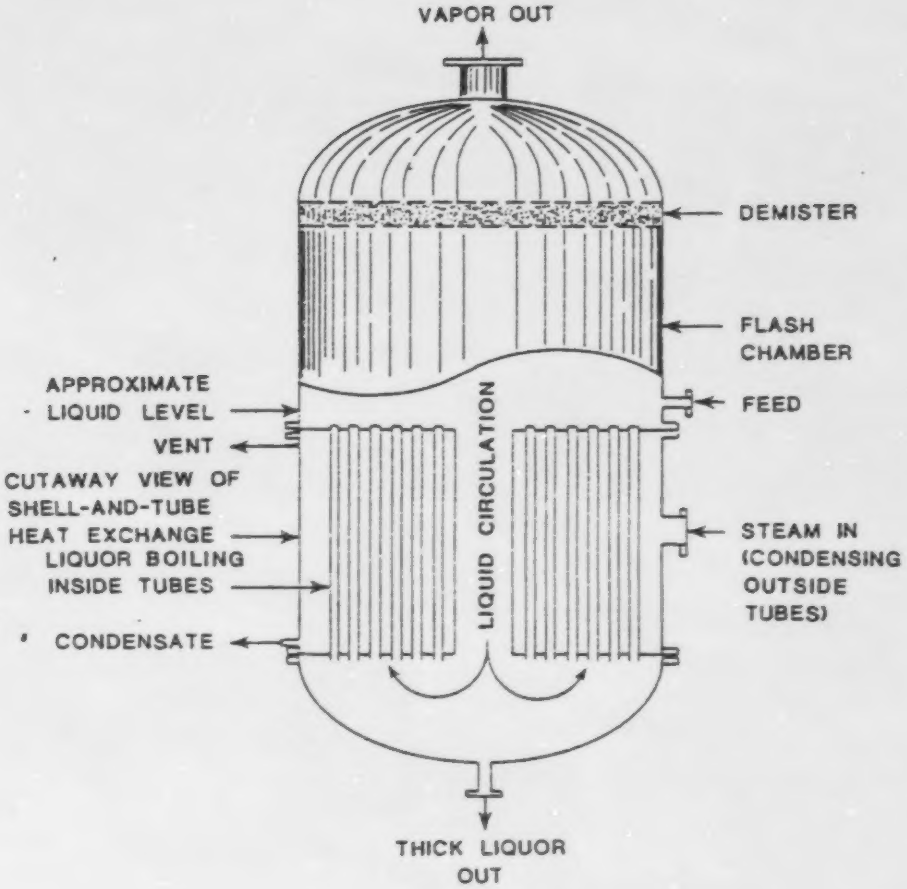

VAPOR OUT
DEMISTER
FLASH CHAMBER
APPROXIMATE LIQUID LEVEL
FEED
VENT
CUTAWAY VIEW OF SHELL-AND-TUBE HEAT EXCHANGE
LIQUOR BOILING INSIDE TUBES
LIQUID CIRCULATION
STEAM IN (CONDENSING OUTSIDE TUBES)
CONDENSATE
THICK LIQUOR OUT

Figure 23-2-6. Short vertical-tube (calandria or standard) evaporator.

The concentrated liquid (the thick liquor) is drawn off the bottom of the evaporator. Occasionally, this liquor may become too concentrated, causing solids to precipitate from it. These solids may plug the drain lines. Use of

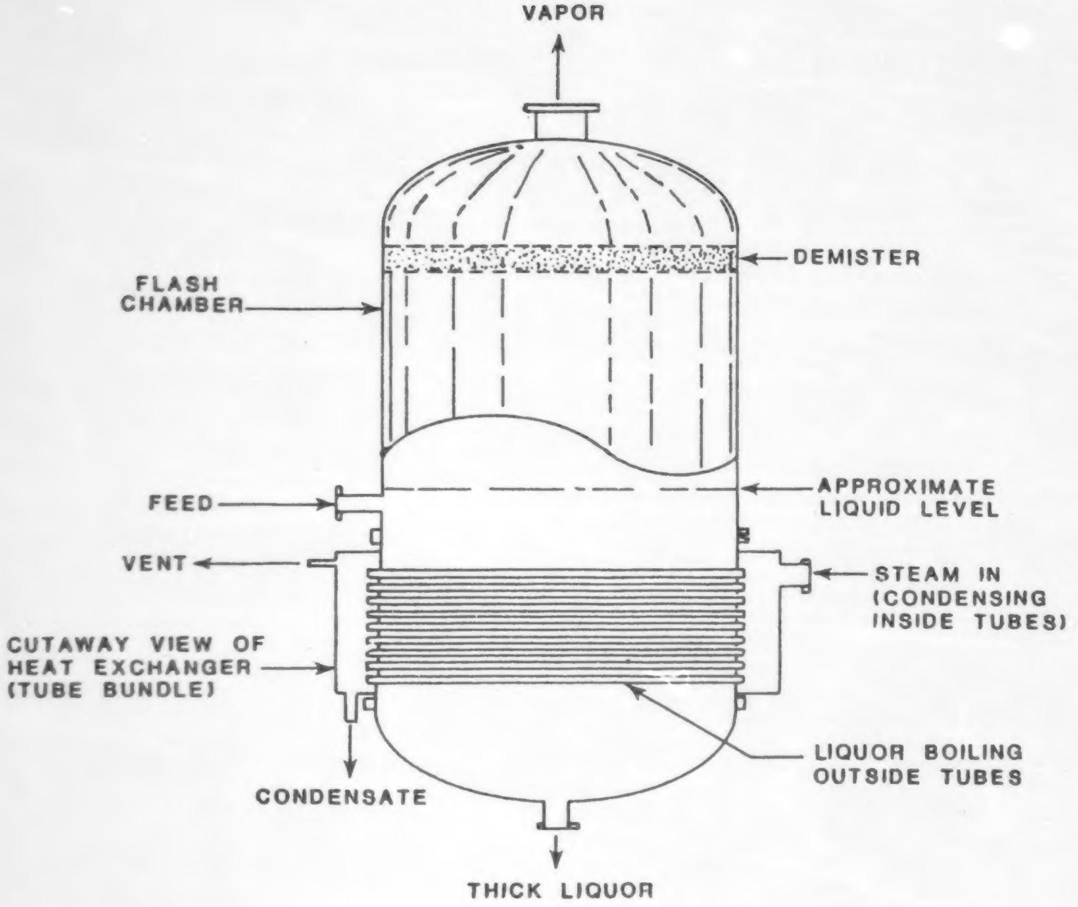

VAPOR
DEMISTER
FLASH CHAMBER
APPROXIMATE LIQUID LEVEL
FEED
VENT
STEAM IN (CONDENSING INSIDE TUBES)
CUTAWAY VIEW OF HEAT EXCHANGER (TUBE BUNDLE)
LIQUOR BOILING OUTSIDE TUBES
CONDENSATE
THICK LIQUOR

Figure 23-2-7. Horizontal-tube evaporator (classic construction).

the turbulent-film evaporator (Figure 23-2-8) can overcome this problem. This type of evaporator continuously scrapes the inner wall with rotating blades, removing the film of solids.

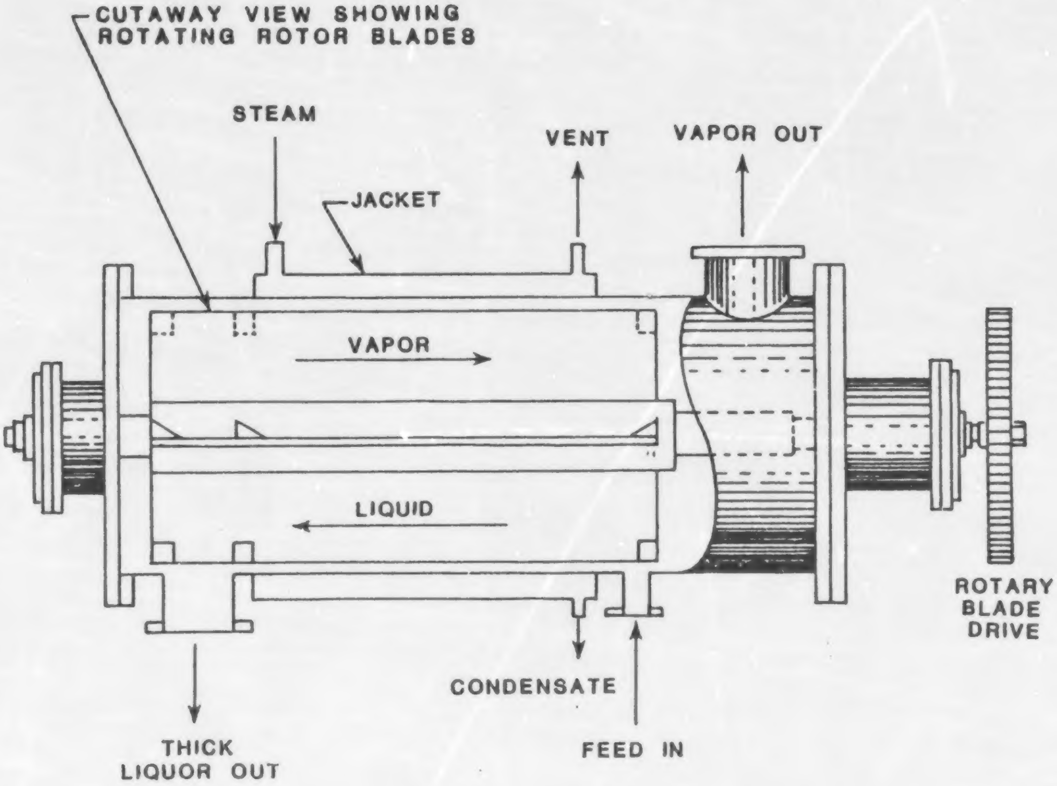

CUTAWAY VIEW SHOWING ROTATING ROTOR BLADES
STEAM
VENT
VAPOR OUT
JACKET
VAPOR
LIQUID
ROTARY BLADE DRIVE
CONDENSATE
THICK LIQUOR OUT
FEED IN

Figure 23-2-8. Turbulent-film evaporator.

Thermosiphon evaporators (Figure 23-2-9) are used to concentrate the intercycle and product streams in the PUREX process.

Heating tubes are mounted outside the pot in the evaporator depicted in Figuer 23-2-9. Feed enters the bottom of the heater section and rises through steam-heated tubes, where it boils. The vapor rises, carrying entrained liquid, and rushes into the flash chamber where it strikes a series of baffles that cause the vapor to change directions and the liquid to fall out of the stream. The thick liquor is drained off at the bottom.

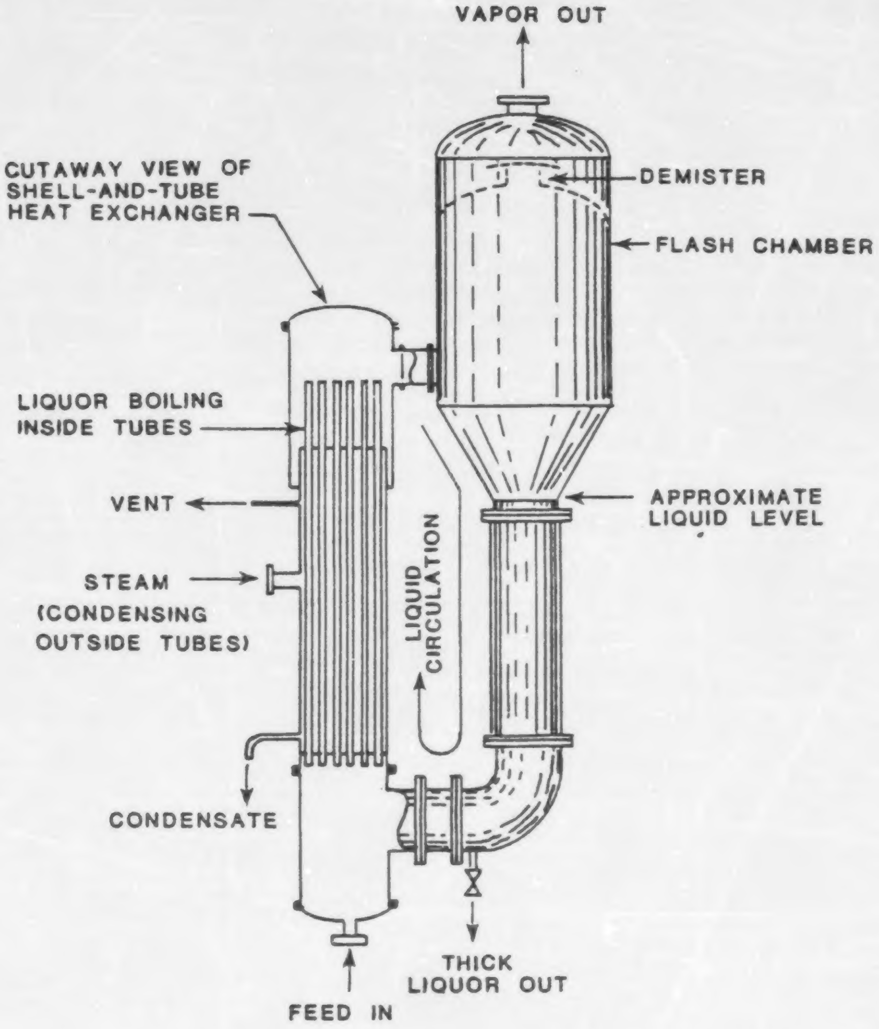

VAPOR OUT
CUTAWAY VIEW OF SHELL-AND-TUBE HEAT EXCHANGER
DEMISTER
FLASH CHAMBER
LIQUOR BOILING INSIDE TUBES
VENT
APPROXIMATE LIQUID LEVEL
LIQUID CIRCULATION
STEAM (CONDENSING OUTSIDE TUBES)
CONDENSATE
THICK LIQUOR OUT
FEED IN

Figure 23-2-9. Long vertical-tube evaporator with external heater and natural circulation (thermosiphon).

EQUIPMENT OPERATION

Evaporators can be operated intermittently, continuously, or semicontinuously. Intermittent operation, called "batch operation," never allows the system to attain steady state; feed and product flows are intermittent. In continuous operations, feed and product flows are constant, and process conditions are at steady state. In semicontinuous operation, vapor and feed flow are constant; but concentrated liquor is drawn off in batches. Semicontinuous or continuous operations usually are employed when a large volume of material is to be concentrated.

Operating procedures vary, depending upon which mode of operation will be used. Table 23-2-3 lists typical operating procedures for each mode of operation.

TABLE 23-2-3. MODES OF EVAPORATOR OPERATION.

Batch	Semicontinuous	Continuous
Procedures: • Charge entire quantity of solution or slurry to evaporator. • Initiate boiling. • Remove, condense and collect vapors continuously. • Terminate evaporation and remove thick liquor when its concentration density or viscosity reaches desired level.	Procedures: • Charge predetermined quantity of solution or slurry to evaporator. • Initiate boiling. • Remove, condense and collect vapors continuously. • Feed solution or slurry to evaporator at a rate approximating its removal. • Continue operation until feed is exhausted or desired concentration of thick liquor is reached. • Remove thick liquor.	Procedures: • Startup same as for semicontinuous mode. • Feed solution or slurry to evaporator at a rate approximating its removal. • Remove thick liquor stream continuously.

EVAPORATION IN THE PUREX PROCESS

In the PUREX process, nitric acid, along with most of the fission products and dissolved solids from the irradiated fuel, leaves the first solvent cycle as high-activity waste in the aqueous waste stream. The waste is concentrated by evaporation to produce an aqueous solution that contains 1.83 M uranyl nitrate, 0.97 M nitric acid, and plutonium nitrate. A volume of 1.6 M sodium nitrite is added to make the solution 0.03 M in nitrite ion. Vapor that results from evaporation of the aqueous stream contains nitric acid and nitrous oxides. This vapor is converted by fractionation to about 60 weight percent HNO_3 for reuse in the solvent extraction process.

The organic intercycle uranium stream is the next to be evaporated. This organic phase, containing the bulk of the uranium at 0.323 M uranyl nitrate and 0.06 M nitric acid, is stripped in a stripping column with 0.01 M nitric acid. After concentration by the evaporator, it forms a solution of 1.5 M uranyl nitrate and 0.29 M nitric acid.

The second cycle waste stream is the third stream to be evaporated, and the solution passes through additional cycles of solvent extraction until desired purity is reached. Finally, the product uranium and plutonium streams are evaporated. Ion-exchange operations provide the final separation of fissionable materials.

EXERCISES

1. A number of commercial ion-exchange resins currently are available. Consult some of the references at the end of this module and other material, and make a list of at least five of these resins. Include name of the resin, its type, its effective operating pH range, the ionic form, the dry- and wet-exchange capacity, and some examples of typical applications.
2. How are trace quantities of fission products removed from the ion-exchange resin employed in the plutonium concentration process? Why is this substance used?
3. Make a list of other applications of sorption processes in nuclear chemistry. How are these processes similar to the processes described in this module?

MATERIALS

175 mg $K_2Cr_2O_7$ in 100 ml H_2O.
1 N NaOH.
1 N H_2SO_4.
IR45 ion-exchange resin.
Distilled water.
1-in OD x 7/8-in ID Pyrex glass tube.
2 glass wool plugs.
Pyrex $P_5$2 No. 7282 stopcock.
5/16-in OD tube.

PROCEDURES

1. Weigh out 35 g of IR45 ion-exchange resin.
2. Place resin in glass column, as in Figure 23-2-10.

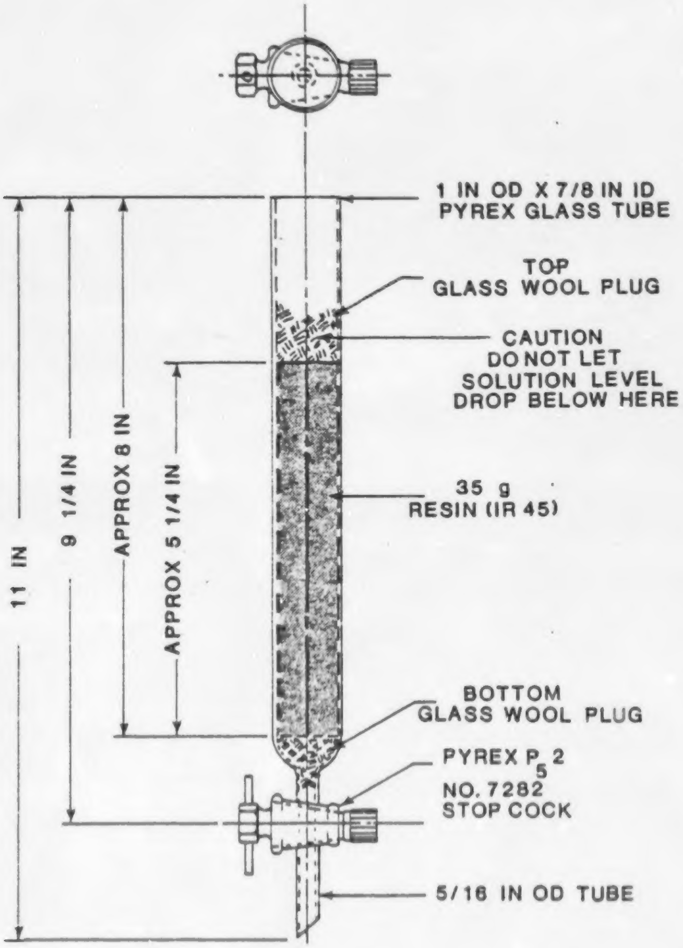

1 IN OD X 7/8 IN ID
PYREX GLASS TUBE
TOP
GLASS WOOL PLUG
CAUTION
DO NOT LET
SOLUTION LEVEL
DROP BELOW HERE
35 g
RESIN (IR 45)
BOTTOM
GLASS WOOL PLUG
PYREX P5 2
NO. 7282
STOP COCK
5/16 IN OD TUBE
11 IN
9 1/4 IN
APPROX 8 IN
APPROX 5 1/4 IN

Figure 23-2-10. Ion-exchange column.

3. Pour distilled water over resin bed until column is full.

4. Open stopcock at bottom of column; practice adjusting flow to 2 drops per second. CAUTION: AT NO TIME DURING OPERATION OF AN ION-EXCHANGE COLUMN SHOULD LIQUID LEVEL DROP BELOW THE UPPER GLASS WOOL PLUG.
5. Add a portion of the 175 mg of $K_2Cr_2O_7$ solution to ion-exchange column; adjust flowthrough to 2 drops per second. Catch effluent in a 250-ml beaker. Effluent should be clear.
6. Continue to add remaining $K_2Cr_2O_7$ solution until first sign of color appears at stopcock. The column is in a "breakthrough" condition.
7. Estimate amount of $K_2Cr_2O_7$ liquid remaining above column and in original beaker.
8. Calculate loading on the column by the following equation:

$$(100 - \text{ml } K_2Cr_2O_7 \text{ solution remaining}) \times 1.75 \times 0.74 = \text{mg } Cr_2O_7^{=} \text{ on column.}$$

9. Add 1 N NaOH to column; adjust flow to 2 drops per second. Continue adding until effluent is clear. The column has now been "stripped."
10. Add 150 ml of 1 N H_2SO_4 solution to column at a rate of 2 drops per second. The column is now in a "regenerated" condition.

Loading	$(R_3NH^+)_2SO_4^= + CrO_4^= \longrightarrow (R_3NH^+)_2CrO_4^= + SO_4^=$
	$(R_3NH^+)_2SO_4^= + Cr_2O_7^= \longrightarrow (R_3NH^+)_2Cr_2O_7^= + SO_4^=$
Regeneration Caustic Elution	$(R_3NH^+)_2Cr_2O_7^= + 2\ NaOH \longrightarrow (R_3NH^+)_2CrO_4^= + Na_2CrO_4 + H_2O$
	$(R_3NH^+)_2CrO_4^= + 2\ NaOH \longrightarrow 2R_3N + Na_2CrO_4 + 2\ H_2O$
Acid Conditioning	$2\ R_3N + H_2SO_4 \longrightarrow (R_3NH^+)_2SO_4^=$

DATA TABLES

None.

REFERENCE MATERIALS

Berg, E.W. *Physical and Chemical Methods of Separation*. New York: McGraw-Hill Book Co., 1963.

Dean, J. *Chemical Separation Methods*. New York: Van Nostrand Reinhold, 1969.

Peterson, S. and Wymer, R.G. *Chemistry for Nuclear Technology*. Palo Alto, CA: Addison-Wesley Publishing Co., 1963.

Staff of the Pilot Plant Section, Oak Ridge National Laboratory. *A Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operations*, Vol. II. Oak Ridge, TN: Oak Ridge National Laboratory, June, 1976.

TEST

SECTION I: MATCHING

Match terms in Column A with definitions in Column B.

Column A

______ Demister.

______ Evaporation.

______ Sorption.

______ Ion-exchange capacity.

______ Ion-exchange resin.

______ Cation-exchange resin.

______ Anion-exchange resin.

______ Ion exchange.

Column B

A. Reversible interchange of ions between a liquid phase and a solid material.

B. Interchange of ions between two resins.

C. Any process by which one substance takes up and holds the molecules of another.

D. A polymerized insoluble electrolyte of high molecular weight.

E. Include sulfonic acid derivatives.

F. Include polyamine compounds.

G. Ability to take up counter ions in a unit volume or weight of a resin.

H. Ability to give off ions per unit volume or weight of a solution or solid.

I. Means of concentrating a solution by boiling away the solvent from the solutes.

J. Used to add caustic soda to aqueous waste stream.

K. Contains baffles to remove entrained liquid.

L. Direct vaporiation of a solid and subsequent condensation of the vapor to the solid state.

SECTION II: MULTIPLE CHOICE

Choose the best response(s) to the following questions and statements:

1. Ions are eluted from a cationic resin by contacting of the resin with:
   a. A strong acid.
   b. A complexing agent.
   c. A hydroxyl complex.
   d. A weakly, basic solution.

2. Efficiency of the anion plutonium sorption process improves if temperature of the solution and resin is approximately –
   a. 60°C.
   b. 50°C.
   c. 30°C.
   d. 10°C.

3. Neputnium, uranium, fission products, corrosion products, and salting agents can be scrubbed from plutonium loaded resin with –
   a. 0.5 M nitric acid.
   b. 7 M nitric acid.
   c. Ferrous nitrate and hydrazine in nitric acid.
   d. 0.35 M sulfonic acid.

4. Anionic-exchange resins are produced by introduction of ______________ into the resin structure.
   a. Amine groups.
   b. Acids.
   c. Copolymerized polystyrene.
   d. Divinylbenzene.

5. Cross-linking of polymer chains causes the chains –
   a. To become more rigid.
   b. To become more soluble.
   c. To fill with water faster.
   d. To swell during the sorption cycle.

6. Operating exchange capacity of a resin usually is ____________________ theoretical capacity.
   a. Lower than.
   b. Higher than.
   c. The same as.

7. In the PUREX process, evaporated streams are –
   a. High-activity waste from the first solvent cycle.
   b. Intercycle uranium stream.
   c. Second cycle waste.
   d. Product uranium and plutonium streams.

SECTION III: ESSAY

8. Write equations that describe a typical anion and cation exchange.

9. Explain purification of plutonium by anion exchange, detailing the feed adsorption, decontamination wash, and product removal steps by constructing a flow chart for each of them.

10. Describe recovery of plutonium by cation exchange.

11. List factors that may cause degradation of ion-exchange resin.

12. Describe ion-exchange operations. Include the following:
    - Operation of a typical column.
    - Provisions for criticality and radiation safety.
    - A general description of the Higgins quasi-continuous contactor.

13. Describe operation of a typical evaporator.

14. List operating procedures for intermittent, semicontinuous, and continuous evaporator operation.

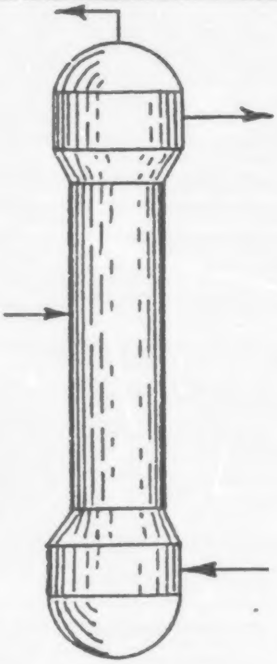
NUCLEAR TECHNOLOGY

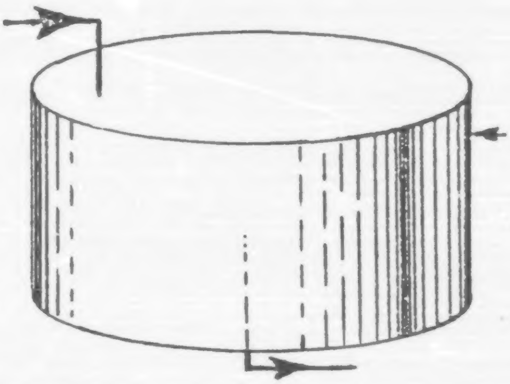
MODULE 23-3

SOLVENT EXTRACTION

NUCLEAR CHEMICAL PROCESSES

COURSE 23





CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

Uranium, plutonium, and the other transuranium elements are separated from the fission products and metallic impurities of spent nuclear fuel by a solvent extraction process. This process achieves separation of these substances by treatment with a selective organic solvent and has been used since the beginning of the nuclear program in the United States, when the PUREX (Plutonium Recovery and Extraction) process was developed to recover plutonium and its parent uranium from a nitric-acid solution of spent fuel. Since then, other processes have been developed to separate the valuable fuel materials from other types of spent fuel.

This module describes the theory, chemistry, and application of the solvent extraction process. The types of lab equipment and process monitoring equipment are described, and the operation of a solvent extraction plant from start-up to shutdown is detailed. The module also contains information on nuclear criticality safety and radiation contamination control in a solvent extraction plant.

MODULE PREREQUISITES

The student should have completed a course in chemistry; Course 2, "Radiation Protection I"; Course 11, "Radiation Detection and Measurement"; Course 17, "Radiation Protection II"; Course 20, "Radiation Monitoring Techniques"; and Modules 23-1 and 23-2.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    - Distribution coefficient.
    - Immiscible liquid.
    - Extraction factor.
    - Extraction.
    - Aqueous feed.
    - Salting agent.
    - Self-salting.
    - PUREX process.
    - Solvent extraction contactors.
    - THOREX process.
    - Solvent recovery system.
    - Mixer settler.
    - Centrifugal contactor.
    - Pulse column.
    - Flooding.
    - Entrainment.
    - Geometry control.
    - Mass and concentration control.
    - Fixed poison.
    - Soluble poison.
2. State the distribution coefficient of 30% tributyl phosphate in a solution of normal dodecane.
3. Describe how a selective organic solvent can be utilized in the extraction of heavy metals from an aqueous solution.
4. List the physical properties of tributyl phosphate and normal dodecane that make these substances useful in the solvent extraction process.

5. Describe the degradation products of tributyl phosphate and normal dodecane and the scheme utilized to purge these products from the system.
6. Describe the composition of the aqueous feed to the PUREX process.
7. Describe the effect of temperature and the concentration of tributyl phosphate and nitric acid in the organic and aqueous phases on the distribution coefficient of uranyl nitrate.
8. List the valence states of plutonium discussed in the module in the order of their relative extractability, and describe methods for the transfer of plutonium from one phase to the other.
9. Sketch a typical PUREX and THOREX flow sheet, and describe the processes.
10. Sketch and describe a typical pulse column contactor, and describe its operation.
11. Describe monitoring and sampling equipment for the solvent extraction process.
12. Describe startup, steady state, and shutdown solvent extraction procedures.
13. Discuss provisions for nuclear criticality safety and control of radiation and contamination in a solvent extraction plant.

THE SOLVENT EXTRACTION PROCESS

As early as 1872, scientists noted that, if a substance is soluble in two immiscible liquids (liquids that will not mix together to form a homogenous solution), it dissolves in both and distributes itself between the two liquid phases in a definite and predictable manner, thus establishing a distribution equilibrium. This equilibrium is described in terms of the ratio of concentration of the solute dissolved in each of the two liquid phases. The ratio is known as the "distribution coefficient" (DC), and often is defined as in Equation 23-3-1:

$$DC = \frac{C_o}{C_a}$$

Equation 23-3-1
(Equation = Eq.)

where:

DC = distribution coefficient (after a sufficient contact period).

C_o = concentration of the solute in the organic phase.

C_a = concentration of the solute in the aqueous phase.

If the volumes of the phases are known, the amount of solute in each phase can be calculated. These amounts may be stated as a ratio, known as the "extraction factor" (EF), which is the product of the DC and the ratio of the organic phase volume to the volume of the aqueous phase. The EF may be utilized as a measure of the efficiency of a specific solvent extraction process using a specific extractant (usually an organic hydrocarbon such as tributyl phosphate, diluted by the solvent). The solvent extraction process consists essentially of utilization of the extractant to remove the heavy metals from the aqueous solution while leaving the fission products and metallic impurities dissolved in the aqueous phase.

In the PUREX process, tributyl phosphate (TBP) is used as the extractant in an inorganic solvent. TBP selectively dissolves uranium, thorium, neptunium, and plutonium from the water phase, with which it is immiscible. Because of a difference in specific gravity of each of the two solvents, the organic solvent will separate itself and float atop the aqueous solvent. This permits the separation of the two solvents into two distinct phases – with the organic phase containing the majority of uranium and other transuranic elements and the aqueous phase carrying most of the dissolved ionic impurities and fission products. The separated organic phase then is contacted and washed (scrubbed) with a fresh aqueous phase that contains an ammonium nitrate solution in order to remove any remaining trace impurities. This purified organic phase is transferred to a partitioning process in which the heavy metals (uranium and plutonium) are separated from each other in an extraction process that transfers (strips) the plutonium from the organic to the aqueous phase, where it can be purified further or concentrated. This chemical transfer is accomplished by reduction of the plutonium ions to a valence state in which they dissolve primarily in the aqueous phase rather than in the organic phase. After the plutonium is removed, the uranium next is stripped from the organic phase into an aqueous phase that contains very low acidity for further processing. The organic phase, after further purification, then is recycled back into the extraction process.

CHEMISTRY OF SOLVENT EXTRACTION

For the solvent extraction process to be effective for separation and purification of a given material, the proper solvents must be selected. The physical and chemical properties of the solvent must be considered carefully, in particular its flash point, miscibility, viscosity, density, and especially the solvent's stability with regard to nuclear radiation.

Tributyl phosphate (TBP), diluted with normal dodecane (NDD), has proved to be a satisfactory organic phase for the separation of uranium and plutonium. Undiluted TBP has nearly the same density as water, and its distribution coefficient is excessively large. Because of these properties, dilution of TBP with normal dodecane is necessary for the production of a solvent that has satisfactory properties. Table 23-3-1 lists some physical properties of these materials.

TABLE 23-3-1. PHYSICAL PROPERTIES OF TRIBUTYL PHOSPHATE AND NORMAL DODECANE.

	TBP	NDD	30% TBP in NDD
Molecular weight	266.32	170.34	
Flash point, °C	145	78	85
Density, 20°C/20°C	0.9730	0.7847	0.819
Viscosity at 20°C (centipoises)	3.32	1.4216	1.83
Solubility in H_2O (g/liter)	0.39		0.28
Solubility in H_2O in solvent (g/liter)	64		

Because the viscosity of undiluted TBP is high, the undiluted TBP would not move easily through the process equipment and would require an impracticably long period of time to disperse and dissolve in the aqueous phase. Dilution with dodecane decreases the viscosity of the solution and provides a more suitable organic solvent phase. Unfortunately, the addition of dodecane considerably decreases the flash point of the solvent.

Although TBP is a relatively stable compound, it will degrade to lower-weight phosphates in the presence of light and other types of electromagnetic radiation and in the presence of high concentrations of acid. These lower-weight phosphates are insoluble in the organic phase. They normally are removed by being placed in contact with sodium carbonate.

Dodecane can degrade by addition of nitrate groups. The degradation of the TBP-dodecane solution results in a decrease in the extraction of fission products to the aqueous phase, in a decrease in the retention of uranium and plutonium in the organic phase, and the retention in the formation of solids and sludges in the extraction apparatus.

The aqueous phase first introduced into the solvent extraction system is called the "aqueous feed" and consists of the solution produced by the fuel dissolution process. The feed solution contains uranyl nitrate, nitric acid, plutionium (IV) fission products, and metallic impurities. The uranium, plutonium, and nitric acid components of the solution provide the nitrate ion concentration necessary for complete extraction of the uranium and the plutonium. The nitric acid sometimes is referred to as the "salting agent" – the material added to increase the nitrate ion concentration. Uranyl nitrate sometimes is termed "self-salting" since it provides the necessary nitrates itself. The addition of nitrates to the solution drives uranium, plutonium, and other metals from the aqueous phase to the organic phase; this is the "salting" effect.

Uranyl nitrate $UO_2(NO_3)_2$ throws an intense yellow color when dissolved in water or TBP. It dissolves in the TBP-diluent mixture by forming $UO_2(NO_3)_2 \cdot 2$ TBP. The maximum solubility of $UO_2(NO_3)_2$ is about 4.34 g of compound per liter of TBP. The distribution coefficient of the uranyl nitrate is about 4 to 1 and is much higher than that of uranyl sulfate or plutonium nitrate. The distribution coefficient of uranyl nitrate decreases with increasing temperature and varies as the square of the TBP concentration in the organic phase and as the square of the nitrate concentration in the aqueous phase. Small changes in the concentrations of these phases, consequently, will produce much larger changes in the uranium distribution coefficient.

Plutonium is available in a variety of valence states and, therefore, will form a variety of compounds in the solution. Of these, plutonium (IV) nitrate is the most extractable. Plutonium (VI) or plutonyl nitrate, $PuO_2(NO_3)_2$, is about half as extractable as plutonium (IV). Plutonium (III) nitrate is about one thousandth as extractable. This variety of available valence states allows the plutonium (IV) in the organic phase to be transferred to the aqueous phase when the +4 valence is reduced to the +3 valence by addition of a reducing agent such as ferrous sulfamate or hydroxylamine. Plutonium (III) in the aqueous phase also can be transferred to the organic phase if the +3 valence is changed to a +4 by the addition of an oxidizing agent such as sodium nitrate or nitrogen dioxide gas.

THE PUREX PROCESS

The *PUREX* process employs TBP in normal dodecane as the solvent for the separation of products from the nitrate solution of the spent fuel. Nitric acid is the salting agent that provides the high nitrate-ion concentration that promotes extraction of uranium and plutonium. After the first uranium-plutonium extraction cycle, the two elements are separated by plutonium oxidation-reduction reactions.

The PUREX process is conducted inside *solvent extraction contactors* – vessels whose prime purpose is to contain and to mix the organic and aqueous phases and to obtain a rapid rate of transfer from one phase to another. Solvent extraction contactors include pulse columns, mixer settlers, and centrifugal contactors. (Contactors are discussed in detail in a later section of this module.)

Figure 23-3-1 is a typical PUREX flowsheet. The solution from the fuel dissolution process (the aqueous feed) is introduced at an itermediate point in the first extraction column, the HA contactor. Before the feed is introduced, it must be adjusted to the desired concentration of uranium, plutonium, and acid. This adjustment is carried out in a feed adjustment tank (not shown). Since the plutonium in the aqueous feed solution is a mixture of plutonium (VI) and plutonium (IV), the plutonium (VI) is converted to the more extractable isotope (plutonium IV) by the addition of nitrite or by the use of $NO\text{-}NO_2$ gas. A typical feed solution contains 1.8 Mole (M) of uranyl nitrate and 0.95 M of nitric acid, as well as plutonium (IV) and fission products.

As the feed is introduced into the HA contactor, it is met by a rising countercurrent flow of a 30-volume-percent solution of TBP in a dodecane diluent. In this manner, the rising organic phase strips the feed of uranium and plutonium (IV). At the same time, the organic phase is met by a countercurrent descending flow of a concentrated aqueous, nitric acid scrub-stream, which prevents uranium and plutonium from back-extracting and also removes (scrubs) most (but not all) fission products from the organic phase. These fission products, along with ionic impurities and cladding materials, leave the system in the aqueous waste stream.

The organic phase – containing the uranium, some nitric acid, the plutonium, and a small quantity of fission products – flows to the stripping column (HC). A dilute nitric acid flows downward and strips the uranium and plutonium into the aqueous phase. The stripped organic phase is sent to solvent recovery for purification and recycling. The aqueous phase travels to an evaporator, where it is concentrated back up to the original feed solution concentration. Sodium nitrate again is added to convert any plutonium (III) or plutonium (VI), that may have been formed during evaporation, to plutonium (IV). The aqueous feed then is fed into the IA contactor, which is a duplicate of the first extraction (HA) contactor that further decontaminates and scrubs the aqueous feed. The aqueous feed solution again is met by a 30-volume-percent solution of TBP in a dodecane diluent. This organic stream extracts uranium and plutonium from the feed. It is met by a countercurrent flow of concentrated aqueous nitric acid that removes whatever impurities that remain. These impurities pass out of the system into the aqueous waste. The purified organic solution then flows to the IB contactor for partitioning of the plutonium product and the uranium product into separate phases.

The partitioning contactor strips the plutonium (IV) from the organic phase to the countercurrent aqueous phase while keeping the uranium in the organic. The uranium and plutonium products are separated by reduction of the plutonium (IV) to the plutonium (III) valence. As the organic phase enters the IB contactor, it is met by an aqueous stream that contains nitric acid and ferrous sulfamate, a reductant. Plutonium (IV) is reduced to plutonium (III) and is stripped from the organic to the aqueous along with about 1% of the uranium. Since these chemical reactions proceed rather slowly, several contacting stages are provided to ensure that the reduction of the plutonium is complete. The plutonium product then exits the bottom of the contactor in an aqueous stream. The organic phase flows to the IC stripping column where the uranium – which is stripped from the organic phase to the aqueous phase by contact with a dilute nitric acid – exits the bottom of the IC contactor. The organic phase then is sent to solvent recovery for purification and recycling. Both the plutonium and uranium can be purified further. The 1% uranium present in the aqueous plutonium stream is recovered by further treatment with a countercurrent flow of TBP in a dodecane diluent. The product then may be purified further by conversion of plutonium (III) to plutonium (II), and by treatment with an aqueous nitric acid strip.

OTHER SOLVENT EXTRACTION PROCESSES

Other solvent extraction processes have been developed since the initiation of the PUREX process. Table 23-3-2 lists some of them. These processes, basically, are similar to the PUREX process, although different organics and salting solutions are utilized for the different feed solutions. The THOREX process (Thorium Extraction) is similar to the PUREX process and is employed in the separation of ^{233}U and thorium from each other and from fission products. This process is represented schematically in Figure 23-3-2.

The basic feature of the THOREX process is the extraction of throium and ^{233}U. The organic stream, containing the uranium and thorium, is fed to the bottom of a stripping contactor. A stream of dilute nitric acid strips the heavy metals to the aqueous phase. This aqueous solution then is fed into a feed-adjustment tank where, by evaporation, water is removed until the original feed cycle concentration is regained. The resulting concentrated solution of ^{233}U and thorium is transferred to the second cycle extraction column, where the uranium and thorium again are stripped into the organic phase and scrubbed exactly as in the first extraction contactor. The organic phase is fed to a partitioning contactor.

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TABLE 23-3-2. AQUEOUS SEPARATIONS PROCESSES.

Name	Solvent	Salting Agent(s)	Irradiated Feed	Products	Status of Demonstration
Purex	30 vol. % TBP in hydrocarbon	HNO_3	Natural U, Al can	U, Pu	Production
TBP-25	4.5 vol. % TBP in hydrocarbon (hexone in second and third cycles)	$Al(NO_3)_3$, HNO_3	U-Al alloy	Enriched U	Production
TBP-Waste Metal Recovery	20 vol. % TBP in hydrocarbon	HNO_3	Natural U, fission products, Na, $PO_4^{=}$, SO_4^{-} ions (wastes from $BiPO_4$ process	U	Production
Zirconium alloy fuel	10 vol. % TBP in hydrocarbon	$Al(NO_3)_3$, HNO_3	Zr-U alloy (enriched U)	Enriched U	Pilot plant
Stainless steel clad fuel	10 Vol. % TBP in hydrocarbon	HNO_3	Stainless steel clad enriched U	Enriched U	Pilot plant
Halex	30 vol. % TBP in CCl_4	HNO_3	Natural U, Al can	U, Pu	Pilot plant
Thorex	42.5 vol. % TBP in hydrocarbon	$Al(NO_3)_3$, HNO_3	Th, Al can	U-233, Th	Production
Interim uranium-233	1.5 vol. % TBP in hydrocarbon	$Al(NO_3)_3$, HNO_3	Th, Al can	U-233	Production
Redox	Hexone	$Al(NO_3)_3$	Natural U, Al can	U, Pu	Production
Hexone 25	Hexone	$Al(NO_3)_3$	U-Al alloy (enriched U)	Enriched U	Production
Uranium-233	Hexone	$Th(NO_3)_4$, $Al(NO_3)_3$	Th, Al can	U-233	Pilot plant
Butex	Dibutyl ether of diethylene glycol	NH_4NO_3, HNO_3	Natural U	U,Pu	Production
Chelate	Diketone chelate (TTA) in benzene or other solvent	HNO_2	Natural U	Pu	Pilot plant
Diisopropyl carbinol	Diisopropyl carbinol or diisobutyl carbinol	$Th(NO_3)_4$, HNO_3	Th, Al can	Pa	Lab studies
Ether	One or more of the following: pentaether, diethyl ether, butylether	HNO_3	Natural U	U, Pu	Lab studies
Ether	Diisopropyl ether	$Th(NO_3)_4$, $Al(NO_3)_3$	Th, Al	U-233	Pilot plant

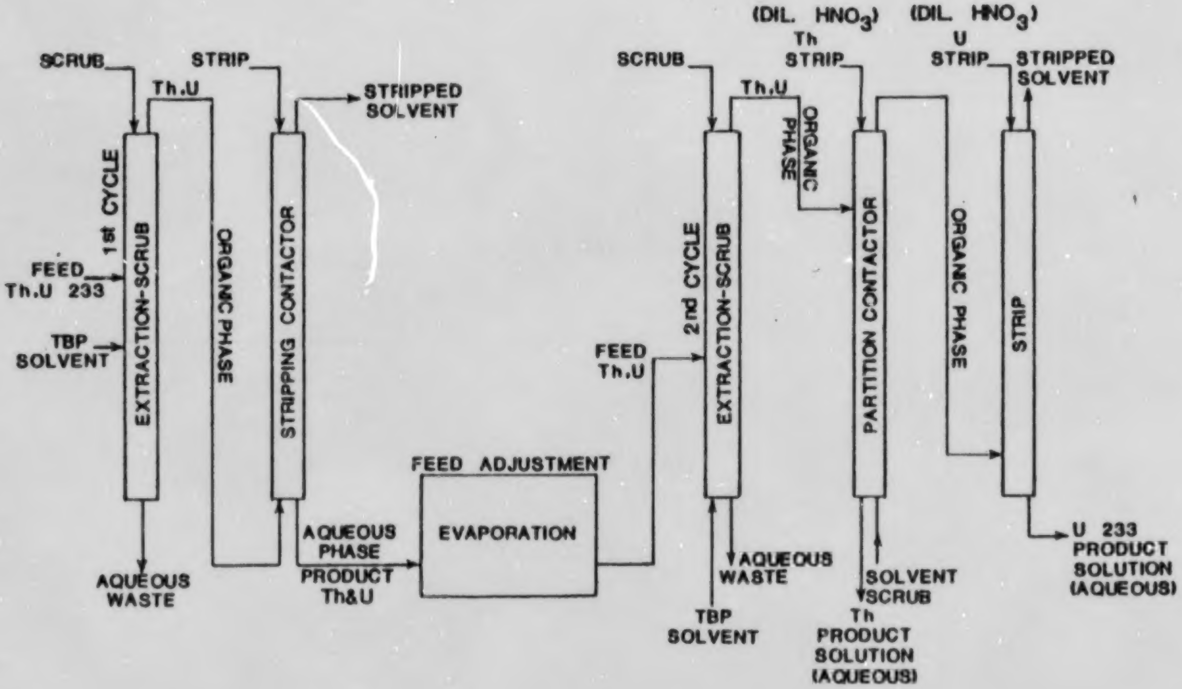
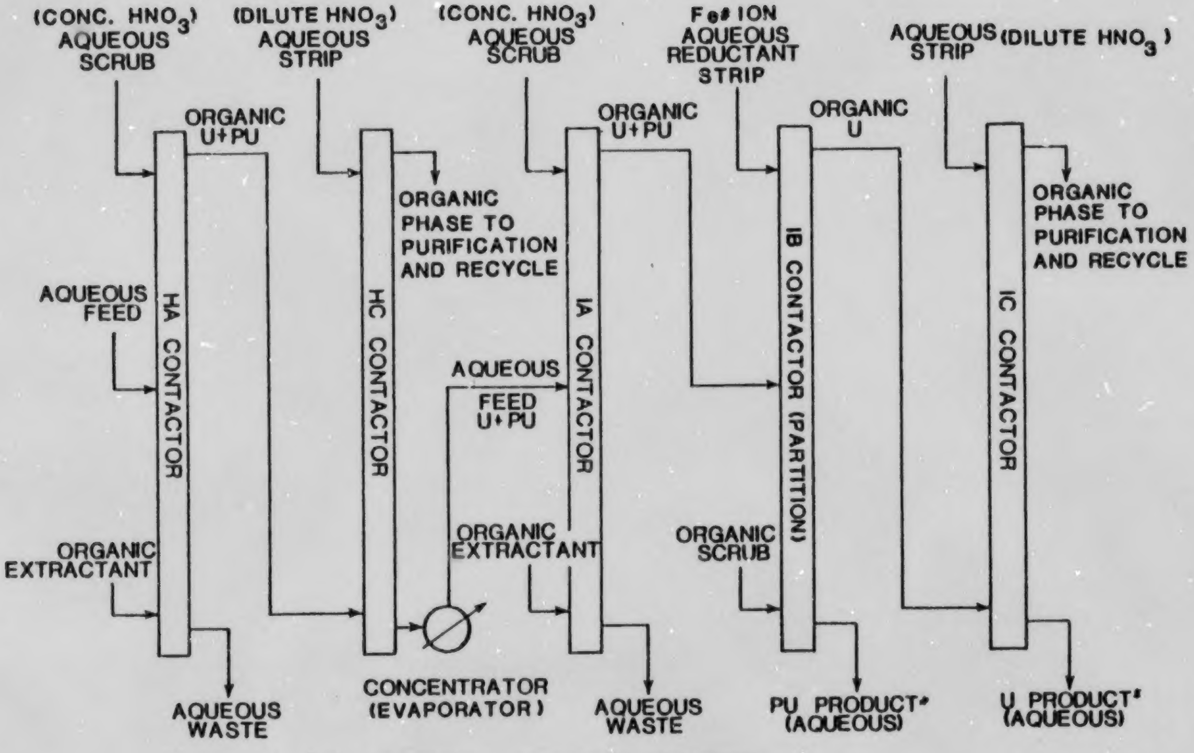

SCRUB
STRIP
Th.U
STRIPPED SOLVENT
1st CYCLE
EXTRACTION-SCRUB
ORGANIC PHASE
STRIPPING CONTACTOR
FEED Th.U 233
TBP SOLVENT
AQUEOUS WASTE
AQUEOUS PHASE
PRODUCT Th&U
FEED ADJUSTMENT
EVAPORATION
FEED Th.U
SCRUB
Th.U
ORGANIC PHASE
2nd CYCLE
EXTRACTION-SCRUB
AQUEOUS WASTE
TBP SOLVENT
(DIL. HNO3)
Th STRIP
PARTITION CONTACTOR
SOLVENT SCRUB
Th PRODUCT SOLUTION (AQUEOUS)
(DIL. HNO3)
U STRIP
STRIPPED SOLVENT
ORGANIC PHASE
STRIP
U 233 PRODUCT SOLUTION (AQUEOUS)

Figure 23-3-2. THOREX flowsheet.

The partitioning cycle separates the thorium from the uranium. The organic solution from the extraction column, containing uranium and thorium, is fed into the partitioning contactor, where it mixes with a dilute nitric acid phase that strips both the uranium and the thorium into the aqueous phase. A solvent (or organic stream) fed into the contactor near the aqueous outlet re-extracts the uranium; and, as a consequence, the aqueous stream leaving the contactor contains only the thorium, while the organic stream carries only the uranium-233. The thorium stream is concentrated for conversion to ThO_2 or Th-metal for use as target material utilized in the production of uranium-233. The uranium-233 contained in the organic phase flows to the stripping column in which stripping is accomplished by contact of the organic phase with a countercurrent flow of dilute (~0.01 $\underline{N}$) HNO_3. The resultant aqueous solution is evaporated to the desired concentration for either storage, ion-exchange processing, third-cycle solvent extraction processing, or conversion to an oxide.

SOLVENT RECOVERY

The TBP used in both the PUREX and THOREX processes is a fairly stable compound but can decompose to lower-weight phosphates in the presence of radiation and high concentrations of acid. The diluent dodecane also can degrade by addition of nitrate groups. A solvent recovery system has been developed to remove the TBP degradation products and to allow the reuse of the TBP. This system is not, however, very effective for removing the nitrated dodecane.


(CONC. HNO3) AQUEOUS SCRUB
(DILUTE HNO3) AQUEOUS STRIP
(CONC. HNO3) AQUEOUS SCRUB
Fe# ION AQUEOUS REDUCTANT STRIP
AQUEOUS STRIP (DILUTE HNO3)
ORGANIC U+PU
ORGANIC PHASE TO PURIFICATION AND RECYCLE
ORGANIC U+PU
ORGANIC U
ORGANIC PHASE TO PURIFICATION AND RECYCLE
AQUEOUS FEED
HA CONTACTOR
HC CONTACTOR
AQUEOUS FEED U+PU
IA CONTACTOR
IB CONTACTOR (PARTITION)
IC CONTACTOR
ORGANIC EXTRACTANT
ORGANIC EXTRACTANT
ORGANIC SCRUB
AQUEOUS WASTE
CONCENTRATOR (EVAPORATOR)
AQUEOUS WASTE
PU PRODUCT* (AQUEOUS)
U PRODUCT* (AQUEOUS)

*TO ADDITIONAL CYCLES, IF REQUIRED

Figure 23-3-1. Sample PUREX flowsheet.

The solvent recovery system contacts the TBP and dodecane solvent with an aqueous solution of sodium carbonate. The degradation products of the TBP and dodecane react with the sodium carbonate to yield sodium phosphate salts. The organic phase then is contacted with dilute nitric acid to remove any residual carbonate. This system succeeds in removing the degradation products from the organic to the aqueous phase, allowing the organic solvent to be reused.

At specified intervals, a more effective cleanup is necessary to remove the minor impurities in the TBP and the diluent not removed by the solvent recovery system. The most effective method of treatment is vacuum distillation.

SOLVENT-EXTRACTION CONTACTORS

Solvent-extraction contactors (SEC) are the heart of the solvent-extraction process. The primary function of the SEC is intimately to mix countercurrent flows to obtain a rapid rate of transfer of metal from one phase to another. This rate of transfer is dependent upon turbulence of the liquids involved and is directly proportional to the contact surface area of the two phases. This area can be increased if each phase is broken into small droplets and intimately mixed. The breaking up of the phases into droplets increases the total surface area of the phase because the total area is inversely proportional to the diameter of the drops: the smaller the drops, the larger the total surface area exposed. This permits a more rapid transfer of metal and a more intimate mixture of the phases.

An elevation view of a mixer settler, a commonly-used contactor, is shown in Figure 23-3-3.

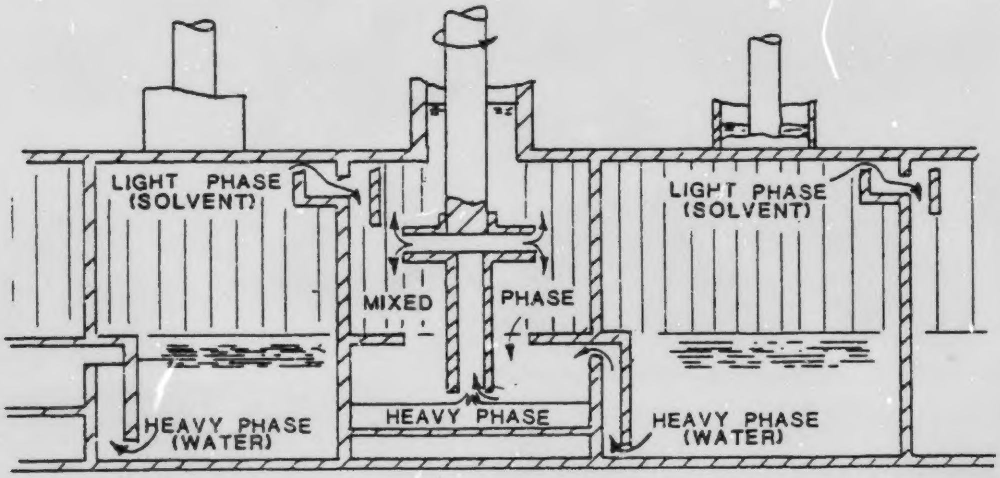

LIGHT PHASE
(SOLVENT)
LIGHT PHASE
(SOLVENT)
MIXED
PHASE
HEAVY PHASE
(WATER)
HEAVY PHASE
HEAVY PHASE
(WATER)

Figure 23-3-3. Elevation view of pump-mix mixer-settler showing three adjacent stages.

Figure 23-3-3 illustrates three stages of a mixer-settler. The mixer disperses the aqueous heavy phase (which enters through the bottom) into the organic light phase and pumps them together into the adjacent settling chamber in which the phases separate. The sequence would be repeated as many times as necessary to achieve the degree of decontamination and separation desired.

The centrifugal contactor is a special type of mixer-settler that makes use of centrifugal force instead of gravity to separate the dispersion into two liquid phases. This design is not used as often as the third type of contactor, the pulse column.

Within the commercial field, pulse columns have been employed more than any other type of contactor in the reprocessing of irradiated fuel. A pulse column is a vertical tower that contains perforated plates spaced along its height. The plates typically are suspended two inches apart; and liquid is pulsed through the column at a one-inch amplitude in such a manner that, with each pulse, the liquid travels one-half the distance of the plate spacing. Application of the pulsing motion to the liquid causes drops of one phase to form in the other phase as the flow is forced through the perforated plates. The normal pulse rate is 50 to 80 cycles per minute, with each phase entering at one end of the column and leaving at the other, thus achieving a countercurrent flow. Figure 23-3-4 illustrates a typical solvent extraction pulse column with extraction and scrubbing sections.

This column consists of a vertical pipe equipped with perforated discs two inches center-to-center. In addition to this shell, the column is provided with feed distributors, phase-disengaging sections, interface-control instrumentation, internal fittings, inlet and exit nozzles and piping for solvent feed and scrub inlet and exit, and a pulse generator that provides the pulse. The top-interface dip probes indicated in Figure 23-3-4 are devices for sensing the height of the interface of the two phases. The signal from this sensor controls rate of flow of the aqueous phase from the column to maintain the interface level at the desired position. Disengaging sections at the top and bottom of the column provide necessary time for the phases to separate. Pipes conduct the separated phases to other columns or sections of the system. The top disengaging section provides a place for the organic phase to exit; the aqueous phase exits out the top of the bottom disengaging section. Pulse columns may be as high as 38 feet.

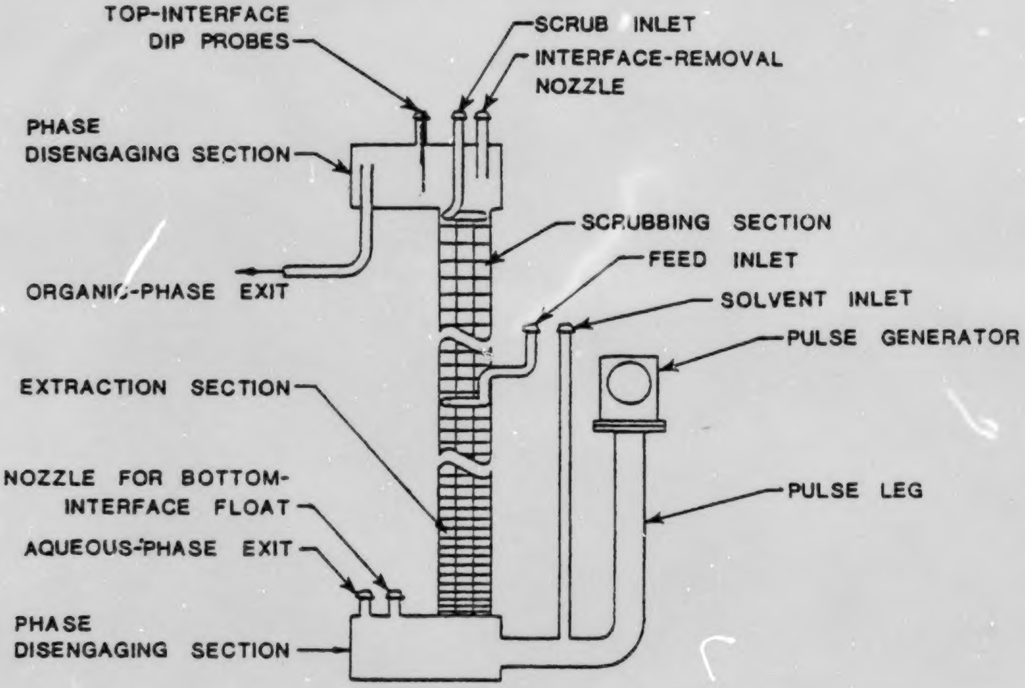

TOP-INTERFACE DIP PROBES
SCRUB INLET
INTERFACE-REMOVAL NOZZLE
PHASE DISENGAGING SECTION
SCRUBBING SECTION
FEED INLET
ORGANIC-PHASE EXIT
SOLVENT INLET
PULSE GENERATOR
EXTRACTION SECTION
NOZZLE FOR BOTTOM-INTERFACE FLOAT
PULSE LEG
AQUEOUS-PHASE EXIT
PHASE DISENGAGING SECTION

Figure 23-3-4. Typical solvent-extraction pulse column with extraction and scrubbing sections.

The perforated plates used to achieve intimate contact of phases in pulse columns usually are assembled to form a single unit that is inserted into the column (Figure 23-3-5).

The plates usually are constructed of stainless steel, although their design and the materials vary with their application in different sections of the system. Plastic plates, for instance, sometimes are employed in the extraction section.

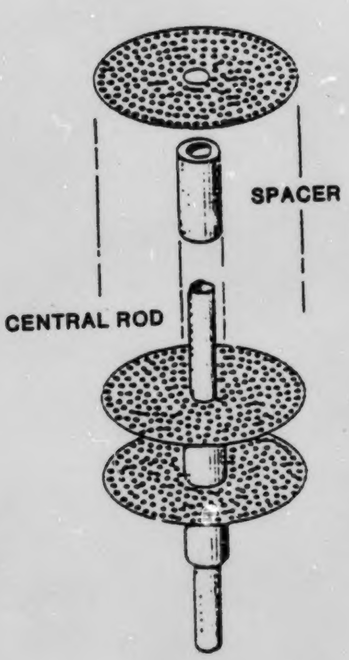


Figure 23-3-5. Exploded view of cartride for a small pulse column.

The pulse generator that provides energy to the pulse column may be either pneumatic or mechanical, although pneumatic pulses are more practical for commercial applications.

AUXILIARY EQUIPMENT

Additional equipment utilized in the solvent-extraction process includes sampling equipment and process monitoring equipment.

The sampling apparatus generally accepted is a hypodermic-needle application in which the solution is lifted from the sampling pot by airlift through a hypodermic into a bottle, and then out through a second hypodermic back into the pot. Such recirculation ensures that the sample is representative.

Process-monitoring equipment includes gamma monitors strategically located to indicate effectiveness of the decontamination. Normally, these monitors are adjacent to the organic line near the top of the extraction column. The monitor must be shielded because of the highly-radioactive sludge buildup at the column interface. The process also is monitored by the withdrawal of flowing-stream or composite samples and by gamma-counting of the effluent streams leaving the columns. Pots equipped with instruments that measure density can determine accurately the concentrations of fissile material stripped by the aqueous stream.

Solvent extraction plants are equipped with equipment that recycles the aqueous and organic phases if process losses are excessive or vessels overflow.

OPERATION OF A SOLVENT-EXTRACTION PLANT

Typical plant operation encompasses startup, maintenance of the process at a steady state, and shutdown.

Empty columns initially are started by introduction of nonradioactive aqueous solutions that contain salting agents. The columns are balanced hydraulically, and the flow-rate is stablilized. An interface between the aqueous and organic phases is established, and only then is the radioactive feed introduced.

A steady state is achieved by establishment of an equilibrium concentration up and down the pulse column. Feed material is removed at the same rate at which it is fed. The correct saturation of the organic with heavy metals must be maintained to provide decontamination from fission products.

Shutdown is accomplished by switching to a synthetic feed of natural uranium or thorium (for the PUREX and THOREX processes respectively) as soon as all the radioactive feed is depleted. The columns then can be shut off at equilibrium.

COMMON DIFFICULTIES IN THE SOLVENT-EXTRACTION PROCESS

Common operating difficulties are flooding and entrainment.

Flooding occurs when the capacity of the contactor is exceeded by excessive flow; by excessive pulse amplitude or frequency; or, in the case of a mixer-settler, by excessive rotational speed. Simply stated, the organic phase entering the contactor is subjected to less pressure via the aqueous inlet than through the contactor. This is also true of the aqueous phase entering the contactor; that is, it would tend to exit via the organic outlet. This condition would be defined by a radical change in the interface controller, since the outlet leg would become light with the organic phase and an overflow of organic solvent from the phase separator in the aqueous outlet line. Prevention or correction can be attained quickly by correction of the flow rates and mixing conditions in such a manner that those conditions fall within the limitations of the contactor system.

Entrainment is the carryover of small droplets of one phase into the other. Normal prevention is maintained through the use of well-designed phase separators at the contactor exits, although it is possible to mix the phases so intimately that an emulsion occurs. The de-entrainment devices do not provide the long hold-up time necessary to permit the emulsion to separate back into its component phases. This emulsification of the mixture when the contactor is operated only with water and organic. Utilization of metallic or ionic impurities eliminates the possibility of an emulsion forming in the contactor. This problem of prevention of emulsification explains the operation of the strip column with a 0.01-N HNO_3 strip solution rather than water.

NUCLEAR SAFETY IN THE SOLVENT-EXTRACTION PLANT

Nuclear safety operations in a solvent extraction plant include nuclear criticality control, control of radiation, and contamination control.

Nuclear criticality safety encompasses every known method of maintaining the solutions in a subcritical state. Criticality safety is especially important because solutions that contain fissile material can become critical much more readily than fissile solid materials.

The three general categories of criticality control are as follows:

- Geometry control.
- Mass and concentration control.
- Use of fixed and soluble poisons.

Geometry control is established when a solution is maintained in a geometry that allows neutrons to escape faster than they can be captured, thus preventing the mass from becoming critical. A primary requisite of the design of pulse columns, collection tanks, and pots is to aid in the establishment of geometry control over the solution.

Mass and concentration control is not used often. Because the concentration of fissile mateial is limited by both equipment design and by administrative edict to below 10 grams per liter, external mass and concentration controls usually are not required.

Poisons are substances that absorb neutrons and, thus, serve to aid in the prevention of criticality within the solution. Fixed poisons usually are an integral part of the vessel, incorporated into the vessel design. An example of a fixed poison would be rings of borosilicate, a neutron-absorbing compound, placed within the vessel. Soluble poisons are those substances added to the reaction solution directly. An example of a soluble poison is cadmium nitrate, which is a neutron-absorbing compound and soluble in the reaction solution.

The normal solvent-extraction process is designed to prevent significant radiation exposure to operating personnel. Primary equipment is installed behind massive shielding. Two shielding designs exist for solvent extraction plants: "canyon" facilities and direct-maintenance facilities.

In the canyon type facility, all maintenance is performed remotely; even the largest vessels, contactors, and pumps can be replaced by use of overhead cranes. Direct maintenance is not permitted. New equipment is brought into the plant by remotely-controlled railroad cars; equipment to be replaced is dropped into the car by crane and taken to a waste disposal system. New equipment is installed by remote devices. This arrangement is safe but, needless to say, expensive.

Direct maintenance facilities are less expensive but are more hazardous. Process equipment is placed inside individual cubicles within the cells. Moving equipment (the euqipment most likely to need maintenance) is located outside the cell wall. After the failed equipment inside a particular cubicle is decontaminated, direct ("hands-on") maintenance is performed.

Process equipment in either type of facility is ventilated through a separate high-vacuum, off-gas system through filters and scrubbers. The cell itself is ventilated through a different off-gas system. The cell is maintained at a slightly higher pressure in relation to the process equipment and at a negative pressure in relation to the environment outside the cell. This arrangement aids in providing contamination control within the facility as well as outside the facility.

EXERCISES

1. Solvent extraction processes are utilized in the extraction of uranium from ore leaches. These ore-recovery processes involve two general types of extractants — acidic alkyl derivatives of phosphoric and pyrophosphoric acids, and high-molecular-weight aliphatic amines. Research these processes, and write a brief description of them. In what ways are they similar to processes described in this module?
2. An alternative to the PUREX process is the REDOX process. Research this process, and list ways in which these processes are similar. Is the REDOX process currently in use in the United States?

MATERIALS

Radioactive iodide solution.
Potassium iodide solution.
Chloroform.
Ferric chloride.
Separatory funnel.
2" diameter 12 to 20 ft high Pyrex glass column with 1/8" diameter, 23% free area pulse plates on 2-in centers.
Pulsing device.
1.0-M HNO_3 aqueous solution.
30% organic solution of tributyl phosphate (TBP).

PROCEDURES

SOLVENT EXTRACTION

This procedure will demonstrate the separation of a radionuclide by the solvent-extraction process.

1. Dilute an aliquot of a radioactive iodide solution with a 10-mg/ml potassium iodide solution. Count the resulting solution in a suitable manner to determine its specific activity; then introduce the solution into a separatory funnel. Insert this value in Data Table 23-3-1.
2. Add an equal volume of chloroform to the separatory funnel.
3. Oxidize the iodide to free iodine by adding dropwise a 5% ferric chloride solution to the funnel.
4. Agitate the funnel to contact the two phases, and extract the iodine into the organic (chloroform) phase of the mixture.

5. Allow the two phases to separate; remove the organic phase from the funnel; and set that phase aside.
6. Add a second equal volume of chloroform to the funnel, agitate, and remove the organic phase from the funnel.
7. Combine the two organic phases, and count the resultant solution in a suitable manner to determine its specific activity. Insert this value in Data Table 23-3-1.
8. Remove the aqueous phase from the funnel, and count the solution to determine its specific activity. Insert this value in Data Table 23-3-1, and compare the results.

FLOODING

1. Construct a 2-inch diameter, 12-to-20 ft high Pyrex glass column with 1/8" diameter, 23% free area pulse plates on 2-in centers.
2. Introduce a 1.0 M HNO_3 aqueous solution at the top of the column and a 30% organic solution of TBP into the bottom of the column. The organic-to-aqueous ratio should be 5/1.
3. Regulate the pulse column at 60 cpm frequency. Determine the flooding capacity at this frequency. Express the flooding capacity in gal/hr/ft^2.

DATA TABLES

DATA TABLE 23-3-1.

	Volume	Specific Activity
Initial aqueous radioactive solution		
Organic phase		
Aqueous phase		

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Peterson, Sigfied and Wymer, Raymond. Chemistry in Nuclear Technology. Reading, MA: Addison-Wesley Publishing Company, 1963.

Staff of the Pilot Plant Section, Oak Ridge National Laboratory. A Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operators, Volume II. Oak Ridge, TN: Oak Ridge National Laboratory, 1976.

TEST

Section I – Matching

1. Match the terms in column "A" with the appropriate term or definition in column "B."

Column A

_____ Distribution coefficient.
_____ Immiscible liquid.
_____ Extraction factor.
_____ Extractant.
_____ Aqueous feed.
_____ Salting agent.
_____ Self-salting.
_____ PUREX process.
_____ Solvent extraction contactors.
_____ THOREX process.
_____ Solvent recovery system.
_____ Mixer settler.
_____ Centrifugal contactor.
_____ Pulse column.
_____ Flooding.
_____ Entrainment.
_____ Geometry control.
_____ Mass and concentration control.
_____ Fixed poison.

Column B

A. Borosilicate rings.
B. Cadmium nitrate.
C. Not often used for criticality control in the solvent extraction process.
D. Allows neutrons to escape faster than they can be captured.
E. Carryover of small droplets of one phase into another.
F. Occurs when capacity of the contactor is exceeded.
G. Employed in reprocessing spent fuel more than any other type of contactor.
H. Special type of mixer-settler.
I. Uses three stages to achieve decontamination.

_____ Soluble poison.

J. Developed to remove TBP degradation products.
K. Used to separate ^{233}U and thorium.
L. Used to contain and mix organic and aqueous flows.
M. Employs TBP as a solvent.
N. Provides material added to increase nitrate concentration.
O. Nitric acid.
P. Measure of efficiency of the solvent extraction process.
Q. Solvent used to extract heavy metals from aqueous nitrate solution.
R. A liquid that cannot be mixed.
S. Ratio of concentrations.
T. Aqueous phase first introduced to the solvent extraction system.

Section II – Essay

2. State the distribution coefficient of 30% tributyl phosphate in a solution of normal dodecane.

3. Describe how a selective organic solvent may be used to extract heavy metals from an aqueous solution.

4. List physical properties of tributyl phosphate and normal dodecane that make these substances useful in the solvent extraction process.

5. Describe the degradation products of tributyl phosphate and normal dodecane and the scheme used to purge these undesirable products from the system.

6. Describe the composition of the aqueous feed to the PUREX process.

7. Describe the effect of temperature and the concentration of tributyl phosphate and nitric acid in the organic and aqueous phases on the distribution coefficient of uranyl nitrate.

8. List valence states of plutonium discussed in the module in the order of their relative extractability; describe methods used to transfer plutonium from one phase to the other.

9. Sketch a typical PUREX and THOREX flow sheet; describe the processes.

10. Sketch and describe a typical pulse column contactor; describe its operation.

11. Describe solvent extraction process monitoring and sampling equipment.

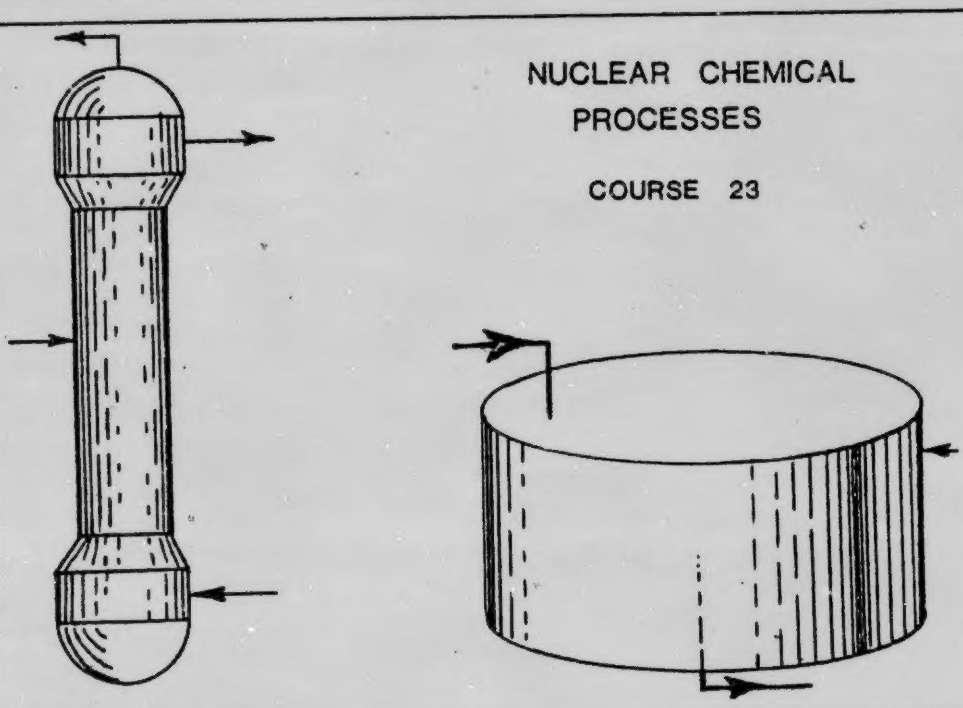
12. Describe startup, steady state, and shutdown solvent extraction procedures.

13. Discuss provisions for nuclear criticality safety and radiation and contamination control in a solvent extraction plant.

NUCLEAR TECHNOLOGY

MODULE 23-4

PRECIPITATION TECHNIQUES AND CENTRIFUGATION



NUCLEAR CHEMICAL
PROCESSES

COURSE 23

CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23	NUCLEAR CHEMICAL PROCESSES
MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
⇨ MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

The reprocessing of irradiated reactor fuel to separate uranium and plutonium from fission products and other spent-fuel impurities can be accomplished in an aqueous medium using one of the following processes:

- Precipitation.
- Ion exchange.
- Solvent extraction.

The precipitation process first was used in laboratory settings to isolate plutonium from uranium and fission products. The process was utilized on a larger scale at Hanford to recover and decontaminate plutonium from irradiated natural uranium fuel elements for use in the Manhattan Project. It was chosen for use in this case because of the simple equipment needed and for the ease with which it could be scaled from the laboratory stage to the production stage. By the mid-1950s, its use was supplanted by the solvent extraction process. The principal disadvantages of the precipitation process are its relatively low yield of plutonium compared to solvent extraction, its large batch rather continuous operation requirement, and the large quantities of radioactive solid waste generated.

This module presents the chemistry of uranium and plutonium upon which the process was based and the precipitation process used at Hanford to recover plutonium. The equipment used to monitor and perform the separation of plutonium are described herein. Particular emphasis on the use and operation of centrifuges for liquid-solid separations is presented. The general safety and contamination considerations for the process also are enumerated.

MODULE PREREQUISITES

The student should have completed a course in chemistry: Course 1, "Radiation Physics"; Course 2, "Radiation Protection I"; Course 17, "Radiation Protection II"; Course 20, "Radiation Monitoring Techniques"; and the first three modules of Course 23.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    - Soluble compounds.
    - Insoluble compounds.
    - Precipitate.
    - Carrier.
    - Internal adsorption.
    - Holdback carriers.
    - Solubilization agents.
    - Decontamination factor.
    - Metal dissolution.
    - Extraction stage.
    - Decontamination cycles.
    - Concentration stage.
    - Isolation stage.
    - By-product precipitation.
    - Product precipitation.
    - Scavengers.
    - Metathesis.
    - Crossover.
    - Heel.

2. State the basis upon which the precipitation process was used to separate plutonium from uranium and fission products.
3. Describe the pertinent chemistry of uranium, plutonium, and the associated fission products.
4. Enumerate and describe the various stages of the precipitation process.
5. Describe feed solutions into the various stages of the processes.
6. Give an overview of plant design and design considerations.
7. Describe the various safety and remote control process devices of importance.
8. Describe the design of solution samplers and their use to ensure that proper solution parameters were maintained.
9. Give an overview of waste solutions from the various stages of the precipitation process.

CHEMICAL PROPERTIES OF IMPORTANCE IN THE PRECIPITATION PROCESS

The bases of the precipitation process are the facts that certain compounds are soluble (can be dissolved) and that other compounds are insoluble (cannot be dissolved) in the same solution. By using this as a chemical basis, plutonium was extracted from natural uranium and fission products at Hanford by alternatively precipitating the plutonium or keeping it in solution by control of its valence. The use of centrifuges is essential to any precipitation technique. The centrifuge was used to separate adequately the insoluble compound, the precipitate, from the solution to form a cake. A centrifuge employs centrifugal force to separate materials of varying densities – in this case, the precipitate and the accompanying solution. The chemical behavior of uranium, plutonium, and fission products that made the process workable are reviewed below.

Uranium is fairly reactive chemically and is soluble in nitric acid to form solutions of $UO_2(NO_3)_2$. For the precipitation process, the uranyl salts (UO_2^{+2}) are important since UO_2^{+2} forms a number of compounds insoluble in aqueous or alkaline solutions. Although few acid-insoluble uranyl compounds are known, uranyl phosphate is fairly insoluble in acid solutions and precipitates slowly when H_3PO_4 is added to an acid solution of uranyl nitrate. Uranyl phosphate will not precipitate from an acid UNH solution containing sufficient SO_4^{-2} to complex the UO_2^{+2}. This fact was used in the extraction phase of the precipitation process (see following sections). Besides hexavalent (uranyl) salts of uranium, tetravalent salts exist; however, U^{+4} is such a strong reducing agent that it is difficult to reduce uranyl to tetravalent uranium. This restricts the usefulness of the precipitation technique to isolate uranium.

In solution, tri-, tetra-, penta-, and hexavalent plutonium can be produced. Only Pu^{+4} and Pu^{+6} are important in the precipitation process. This is true since the pentavalent form is unstable and the trivalent form easily can be converted to the tetravalent form. Hexavalent plutonium customarily is considered to exist as a "plutonyl" ion, PuO_2^{+2}. Plytonyl- and uranyl-ions are similar; however, plutonyl can be reduced to tetravalent plutonium much more easily than uranyl can be reduced to tetravalent uranium.

Tetravalent plutonium forms a number of relatively insoluble compounds, and the hexavalent ion forms very few insoluble compounds. The difference between the solubilities of tetra- and hexavalent plutonium forms the basis for the extraction and decontamination phases of the precipitation process.

In addition to the pertinent chemistry of uranium and plutonium, some other general considerations for the precipitation process need to be reviewed. If an element in solution is not present in a sufficiently high concentration to be precipitated from a solution directly, it can be coprecipitated from solution by the formation of a precipitate of an element present in a higher concentration. The most efficient coprecipitators, referred to as "carriers," are those that have approximately the same crystal lattice parameters. The element to be carried also must form an insoluble compound with the precipitating anion. Although many compounds will carry Pu^{+4} from solution, only bismuth phosphate ($BiPO_4$) and lanthanum fluoride (LaF_3) are of prime importance in the precipitation process as it was performed at Hanford.

Both of these compounds will carry tetravalent plutonium from acid solutions, even when it is present only in very minute traces. Bismuth phosphate carries Pu^{+4} by internal adsorption, in which the trace element is adsorbed on the surface of the carrier as the carrier crystal is growing in the solution. Lanthanum fluoride carries tetravalent plutonium by virtue of the formation of $2\ LaF_3 \cdot PuF_4$ double salt. The efficiency of carrying either of these compounds is dependent upon the conditions of the carrier precipitate. Very few carriers for hexavalent plutonium are known.

Holdback carriers and solubilization agents act to keep a trace element in solution during a precipitation. By addition of such a holdback carrier to the solution, an element that would be carried away now is carried to a lesser extent. For example, if radiolanthanum (a fission product) is carried to the extent of 3% with bismuth phosphate, the addition of a large amount of stable lanthanum to the solution will result in less than 1% of the radiolanthanum being carried. A solubilization agent achieves the same end result by changing the nature of the solution to make the element now hold more soluble in the solution.

THE PRECIPITATION PROCESS

The precipitation process as performed at Hanford Atomic Products Operation was based upon (1) the facts that hexavalent uranium and plutonium form salts that are water-soluble; (2) that many insoluble compounds of tetravalent uranium and plutonium exist; and (3) that plutonium is reduced more readily to the tetravalent state than is uranium. The aim of the precipitation plant was to separate plutonium from the uranium in which it was formed; to remove essentially all the fission products from the plutonium; and to isolate the plutonium in a relatively pure state free of carrier. To produce the plutonium, natural uranium fuel slugs were irradiated in piles for 100-200 days at an average power level of about 250 MW. The fuel slugs then were stored for 40-60 days to allow ^{239}Np to decay in order that its gamma radiation would be only a negligible contribution to the principal activities of longer-lived products of the irradiation. This procedure resulted in a negligible activity in the final isolated plutonium product.

The fission product activity associated with one ton of uranium metal and the associated plutonium must be reduced to a factor of 10^7 before isolation of the plutonium can be performed. Such decontamination allowed the isolation phase of the process to be performed without the large amounts of shielding and the remote controls required in the other portions of the process. This reduction factor of radioactivity – normally referred to as the "decontamination factor," DF, – may be expressed in the form of Equation 23-4-1.

$$DF = \frac{\text{Fission product activity initially present}}{\text{Fission product activity present at a given step}}$$

Equation 23-4-1
(Equation = Eq.)

The basic precipitation process may be broken down into the following operations (see Figure 23-4-1):

- Dissolution of the uranium, plutonium, and associated fission products.
- *Extraction* of the plutonium from the bulk of the uranium in which it was formed.
- Reduction of fission product activity still associated with the plutonium through *decontamination*.
- Further decontamination and *concentration* of the plutonium product with respect to the carrying solution volume and amount of needed carrier agent in the crossover and metathesis cycle.
- The *isolation step*, which frees the plutonium product of carriers and other product impurities.

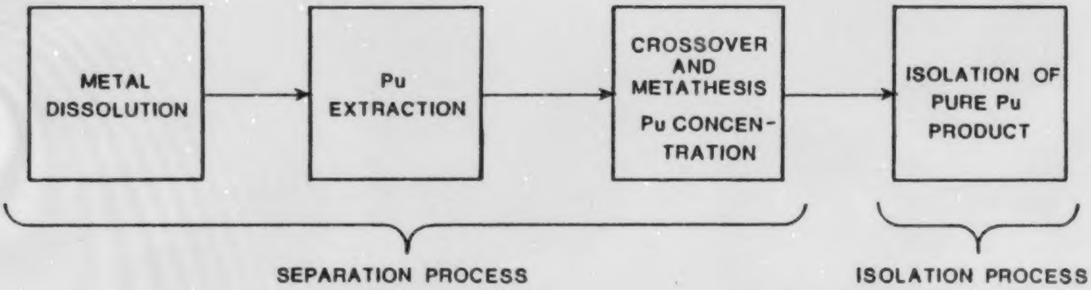
METAL DISSOLUTION
Pu EXTRACTION
CROSSOVER AND METATHESIS
Pu CONCENTRATION
ISOLATION OF PURE Pu PRODUCT
SEPARATION PROCESS
ISOLATION PROCESS

Figure 23-4-1. The precipitation process for the recovery of plutonium from irradiated natural uranium.

The first four steps of the process are regarded as the *separation* process. In the development of the stages of the precipitation process that follows, each step will be described with regard to the processes involved in that particular step, the specific equipment of interest used, and operation of the equipment as necessary.

PLANT DESIGN AND GENERAL EQUIPMENT

The general plant features are described in this section of the module, while more specific features of the equipment will be described as necessary in the description of the process states. The dissolution and extraction stages were carried out in the same building as the decontamination stage of the precipitation process. Design of the building was based upon four considerations:

- Adequate protection of operating personnel from radiation must be ensured.
- Remote operation of the process equipment was essential.
- Remote maintenance of the process equipment was necessary because of high radiation levels.
- Since the Hanford plant was the first to use this process, the design was flexible in order that changes might be made after operation.

The protection of personnel from radiation was a combination of distance and shielding. The net result was equipment operated behind massive concrete walls by remote controls. The dissolution, extraction, and decontamination stages of the process represented no other unusual operating aspects. Maintenance had to be done remotely due to equipment contamination. It was, therefore, essential that no items such as valves and pumps that required periodic maintenance and inspection be incorporated in the design. Items that might leak or drip under normal operating conditions were also undesirable. Therefore, the process piping was designed using single lines without multiple connections, and vessels associated with the process had no bottom outlets. Steam jet ejectors were employed to eliminate the need for pumps.

The most important feature of the remote maintenance condition was the connector that connected pipes, conduits, and instrument leads. (See Figure 23-4-2.) The connector

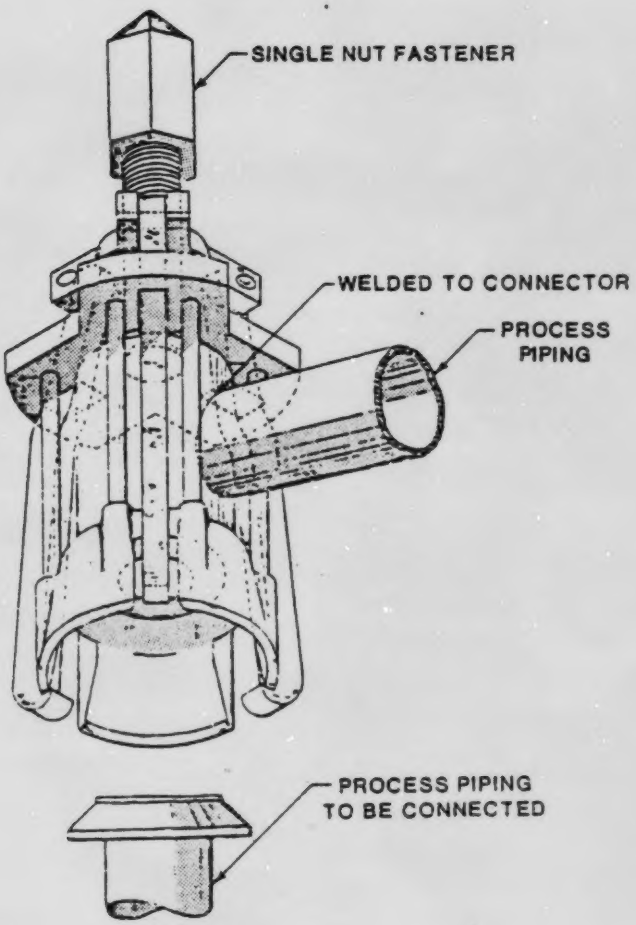
SINGLE NUT FASTENER
WELDED TO CONNECTOR
PROCESS PIPING
PROCESS PIPING TO BE CONNECTED

Figure 23-4-2. Pipe connector for remote maintenance.

could be connected by the tightening of a single nut. This connector was used in all locations exposed to high radiations from process solutions. The connectors were operated using a special electrically-driven impact wrench carried on the building overhead crane. The crane cab was heavily shielded to protect the operator from radiation and was equipped with two periscoeps and television equipment to allow viewing of the plant. The crane was used with a hook in the conventional manner. The transfer steam jet that transferred process solutions is illustrated in Figure 23-4-3.

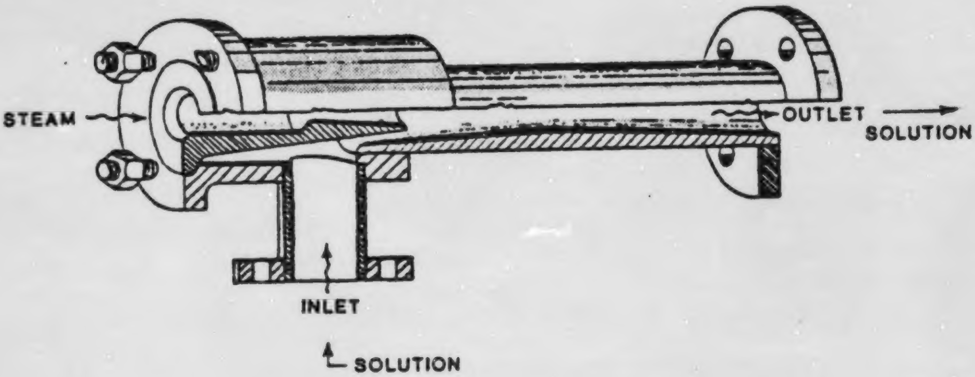

Figure 23-4-3. Transfer jets for transfer of all solutions.

The processes carried out in the separation phase of the precipitation process were performed in a series of identical equipment units. Most of the extraction and decontamination steps were carried out in a standard equipment group (Figure 23-4-4), consisting of a precipitator, a catch tank, a centrifuge, and a solution tank. All processes using this standard equipment group were carried on in standard cells 22 ft high, having walls 7 feet thick and a cover 7 feet thick.

Personnel access to the cell was only through the cover, which had removable sections. The cover sections had stepped interlocking edges in order that no straight penetrations existed in the cover through which the radiation could stream unless some shielding material intervened. These cells housed processes until a decontamination factor of 10^5 was reached.

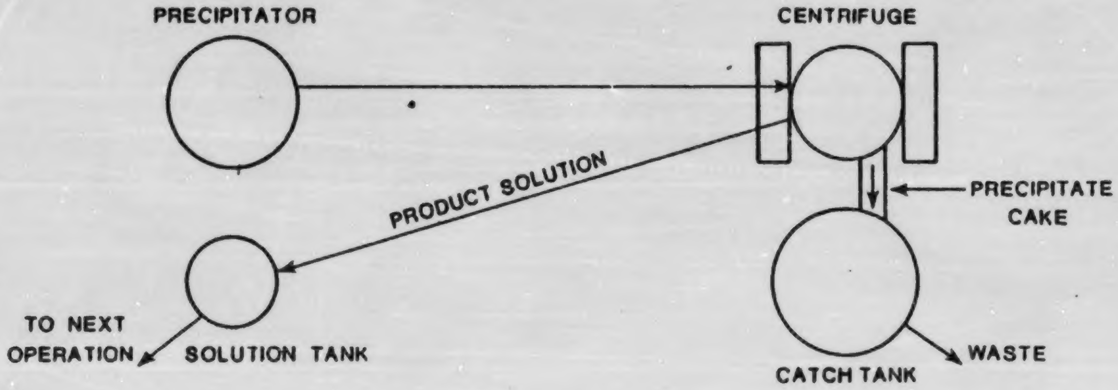

Figure 23-4-4. Standard equipment setup for extraction and decontamination cycles.

Once this level of decontamination was reached, operations were transferred to a building in which the concentration operation occurred. This operation was performed in a more normal type of structural setting. The standard equipment group again was employed in this phase; however, ordinary piping was used. There was still sufficient residual radioactivity present to make some shielding necessary. The shielding requirement was met by a foot of concrete interposed between the process equipment and personnel. Design was such that personnel were at least 10 feet from the process vessels, with the concrete interposed. The final product from the concentration phase was transferred to the isolation operation building with solution transfer cans. Radioactive wastes from the process were brought to a tank farm area and buried in stainless-steel tanks lined with stainless steel. The tanks terminated in a diversion box with which the flow of waste could be changed from one storage tank to another.

Wastes stored in these tanks might eventually have caused the liquid to heat up to boiling, so the tanks were equipped with air-cooled reflux condensers. The isolation operation was performed in a separate building, where plutonium was isolated as a nitrate. The solutions evaporated in the separation step were evaporated to form a viscous plutonium cake.

METAL DISSOLUTION

The first step in the separation of plutonium from uranium and the accompanying fission products was the removal of the aluminum jackets from the irradiated uranium fuel slugs, followed by the dissolution of the metal slugs. (See Figure 23-4-5.) The uranium slugs were loaded remotely into dissolvers, where the coating removal and metal dissolving were carried out in consecutive dissolvers. The dissolvers were ruggedly constructed to withstand the mechanical shocks of metal loading and the severe corrosion conditions. The aluminum jackets were removed by reaction with sodium hydroxide (NaOH) in the presence of sodium nitrate ($NaNO_3$) solution. The $NaNO_3$ prevented the evolution of hydrogen which might have reached an explosive concentration in the dissolver. Part of the silicon alloy that bonded the aluminum and uranium formed in the dissolver

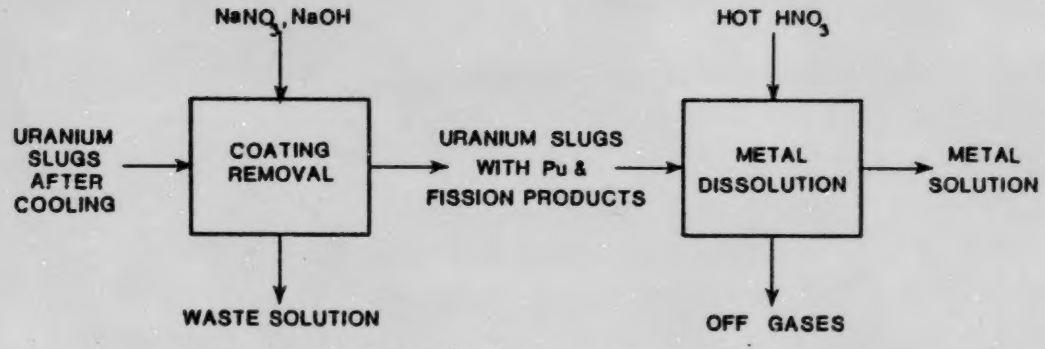
NaNO3, NaOH
HOT HNO3
URANIUM SLUGS AFTER COOLING
COATING REMOVAL
URANIUM SLUGS WITH Pu & FISSION PRODUCTS
METAL DISSOLUTION
METAL SOLUTION
WASTE SOLUTION
OFF GASES

Figure 23-4-5. Metal dissolution process.

a sludge, which was flushed out with the coating removal solution or with water and acid washes following the draining of the coating solution.

The metal was dissolved in batches by addition of nitric acid and by digesting until a desired specific gravity was reached. This step is characteristic of the chop-leach phase of other fuel reprocessing methods. Each batch thus generated was diluted in the dissolver so that the solution was about 55% UNH to prevent crystallization. The batch then was cooled and jetted, where water was added to dilute the solution to approximately 40% UNH. Sulfuric acid then was added to the solution to achieve a certain concentration per metal weight. The solution then was transferred for the extraction.

In the dissolution process, uranium metal was oxidized to uranyl nitrate hexahydrate, which is abbreviated UNH. The plutonium contained in the slugs was oxidized by the nitric acid addition to the +3 or +4 state and formed insoluble nitrates. No appreciable amount of hexavalent plutonium was formed. The metal solution then was stored for the extraction process.

EXTRACTION PROCESS

The plutonium product was extracted from the metal solution, which contained UNH and sulfuric acid (Figure 23-4-6). The metal solution, with the sulfuric acid complexing the uranium to prevent its precipitation as uranyl phosphate, was transferred to a precipitator and further diluted. A pre-extraction treatment was performed with sodium nitrite to ensure that the plutonium was in a tetravalent form that could be carried by a bismuth phosphate precipitation. In this procedure, the reduction to Pu^{+6} to Pu^{+4} occurred, and the oxidization of Pu^{+3} to Pu^{+4} occurred. The extraction precipitate was made by addition of bismuth solution and then phosphoric acid uniformly over a period of time.

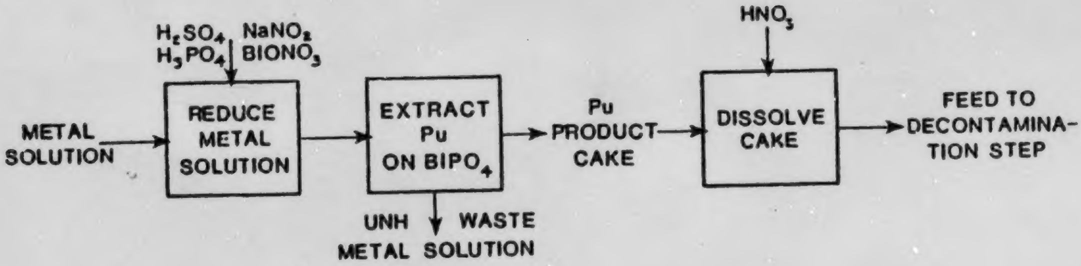
H₂SO₄ NaNO₂
H₃PO₄ BIONO₃
HNO₃
METAL SOLUTION
REDUCE METAL SOLUTION
EXTRACT Pu ON BIPO₄
Pu PRODUCT CAKE
DISSOLVE CAKE
FEED TO DECONTAMINATION STEP
UNH WASTE METAL SOLUTION

Figure 23-4-6. Extraction of plutonium from the metal solution.

After cooling, the slurry was centrifuged and the precipitator and centrifuge washed with water to remove UNH and soluble fission products held up in the precipitator and centrifuged cake. The combined effluent and washings then were stored in the catch tank. They constituted the metal waste solution. About 90% of the fission product activity and less than 1% of the plutonium in the original metal solution was left in the waste metal solution. The cake then was dissolved in nitric acid, and the dissolving was completed by agitation of the solution in the solution tank. A plutonium yield of 90-100% was normal, and the associated fission product in the plutonium solution was less than 10% of the original activity. The plutonium solution was jetted to storage prior to the decontamination processes. The metal waste solution could be worked to extract the uranium from the solution and, if desired, could be reworked to recover the remaining traces of plutonium.

Characteristic of the extraction process, as well as subsequent portions of the stages based on precipitation, was the precipitation tank (Figure 23-4-7), which was equipped with an agitator. A spray distributor was used to wash down the vessel walls to prevent a buildup of bismuth phosphate cake. This jet-operated device pulled liquid up from the tank through a suction leg and forced it back into the vessel through an outer concentric pipe. Two thermometers were used to control the temperature in the precipitator since the temperature was very critical in the precipitations.

The centrifuge illustrated in Figure 23-4-8, used to centrifuge the plutonium cake, operated at either 870 or 1740 revolutions per minute to give an effective centrifugal force of 430 to 1730 times the force of gravity, respectively. The higher speed was employed for the lanthanum fluoride precipitations (see following sections), while the lower speed was sufficient to separate the bismuth phosphate precipitates from the solution in the extraction and decontamination procedures.

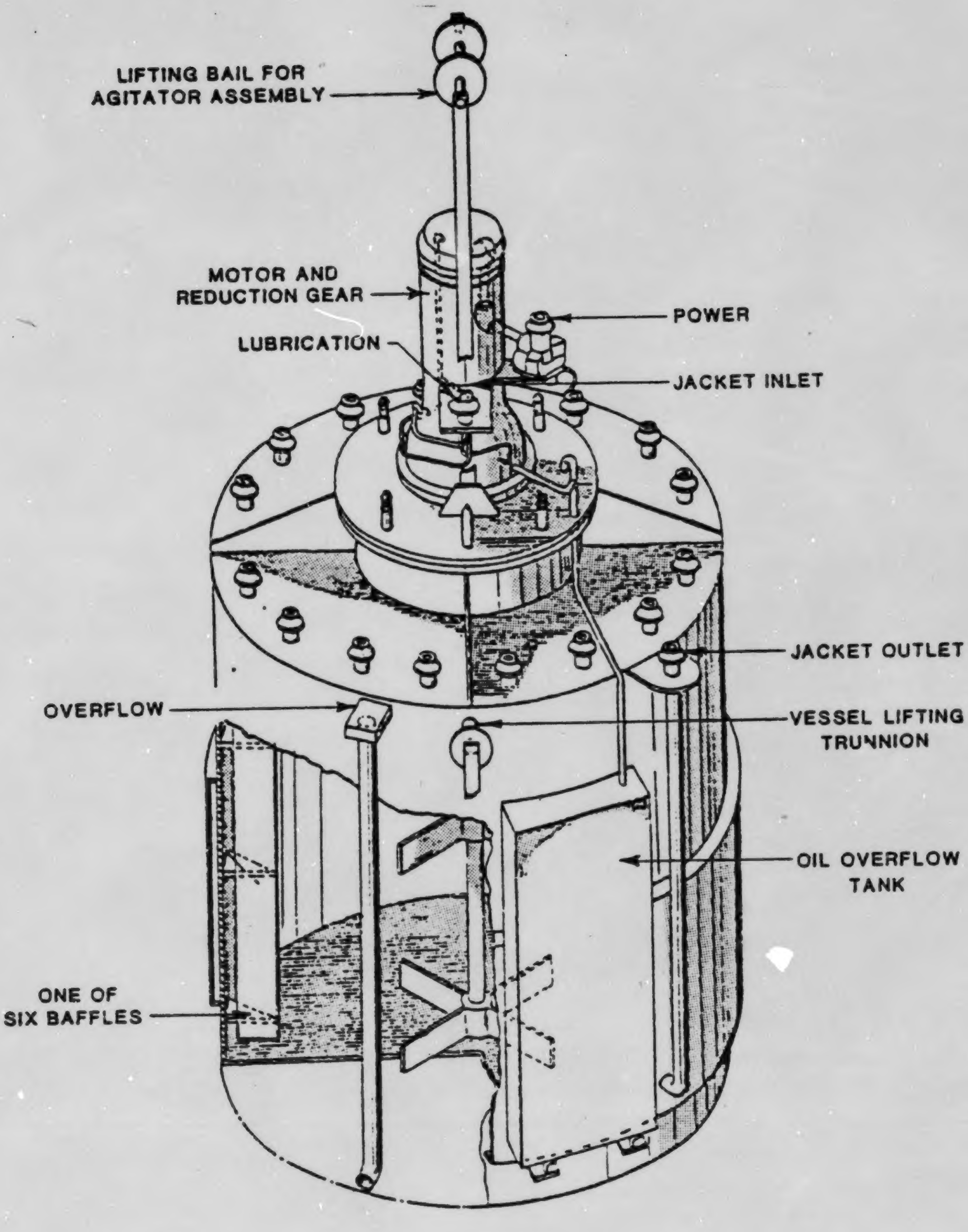
LIFTING BAIL FOR AGITATOR ASSEMBLY
MOTOR AND REDUCTION GEAR
POWER
LUBRICATION
JACKET INLET
JACKET OUTLET
OVERFLOW
VESSEL LIFTING TRUNNION
OIL OVERFLOW TANK
ONE OF SIX BAFFLES

Figure 23-4-7. Precipitator.

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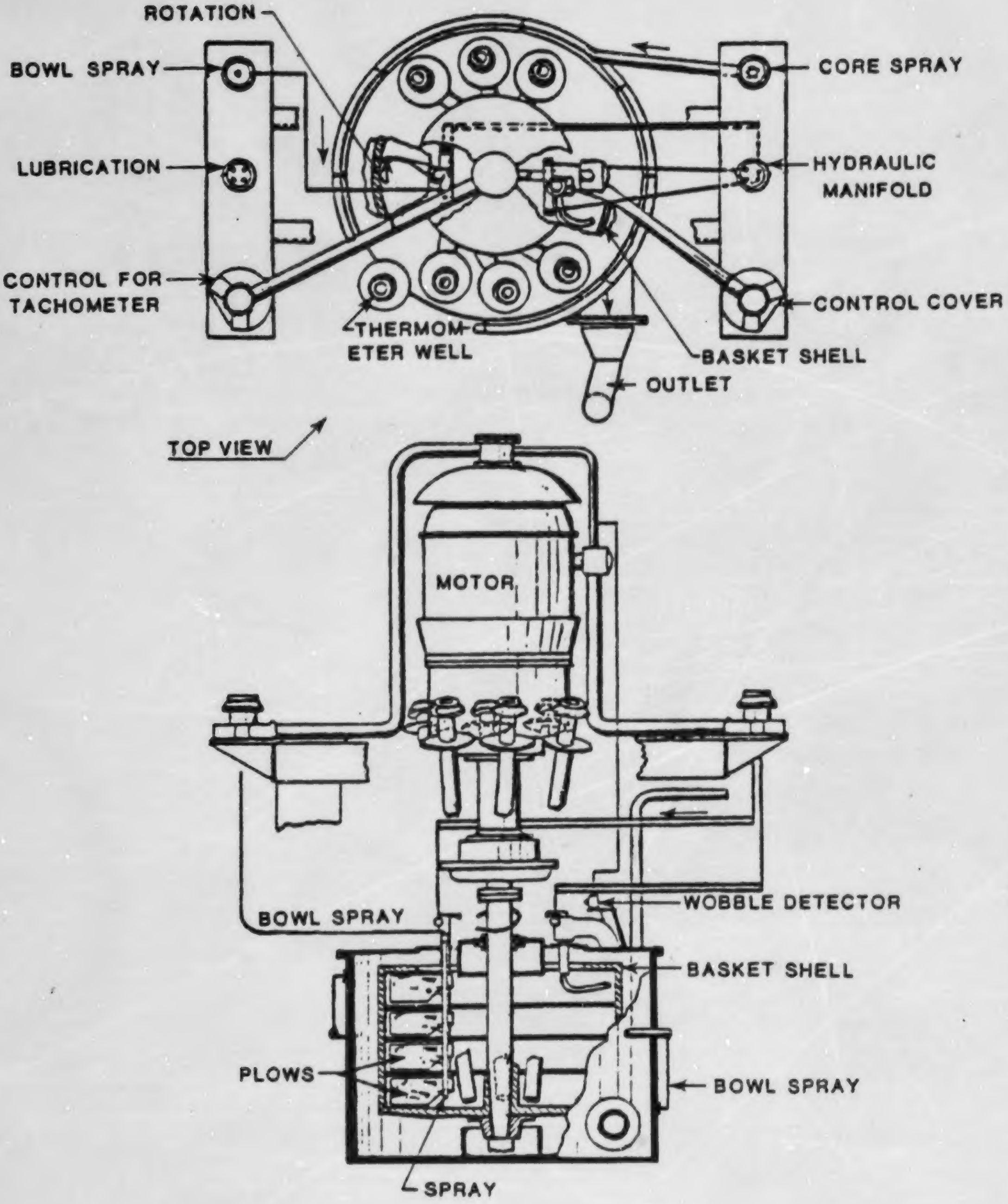
ROTATION
BOWL SPRAY
CORE SPRAY
LUBRICATION
HYDRAULIC MANIFOLD
CONTROL FOR TACHOMETER
CONTROL COVER
THERMOMETER WELL
BASKET SHELL
OUTLET
TOP VIEW
MOTOR
WOBBLE DETECTOR
BOWL SPRAY
BASKET SHELL
PLOWS
BOWL SPRAY
SPRAY

Figure 23-4-8. Centrifuge.

The centrifuge waste solution flowed from an opening near the bottom casing of the centrifuge into the catch tank (Figure 23-4-4). The centrifuge was mounted on concrete blocks so that the waste solution exited by means of gravity flow. To assist in cake removal, two sets of plows were included in the centrifuge design. For cleanup and cake washing, two sprayers were available. These sprayers were operated by pumps outside the process cell. Connections to the centrifuge bowl were made through six sleeves from the cover brought up at a slant to clear the motor assembly. A simple manometer indicated the depth of the liquid or weight factor. A thermometer and microphone connection was made to the top of the centrifuge case. The microphone was used to listen to the operation of the jets and motors, as described in more detail in a later section.

The catch tank was identical in design to the precipitator, but had no agitator. Openings in the top of the catch tank had connections for a liquid level and density recorder, thermometer, sampler, sparger, and the needed lines for these devices. A microphone also was used to listen to outlet steam jets to determine when the jet was gassing, i.e., because a tank was empty. The solution tank was a smaller version of the precipitator, having the same connections and monitoring systems as the catch tank.

DECONTAMINATION CYCLES

The fission product activity still associated with the desired plutonium product was reduced further by processing of the plutonium through two decontamination cycles, as shown in Figure 23-4-9. The fission products were removed largely in a series of alternate precipitations of fission products and plutonium. Advantage was taken of the difference in the solubility of the oxidized and reduced states of plutonium phosphate. Each cycle consisted of two bismuth phosphate precipitations. The first one was performed with the plutonium in a PuO_2^{+2} solution so that it remained in solution; and the second, with a Pu^{+4} solution so that the plutonium was carried on the bismuth phosphate. The precipitation from the oxidized plutonium solution (PuO_2^{+2}) was called the "by-product precipitation" and removed the major portion of the remaining fission products. The by-product precipitation left many phosphate-soluble fission products in solution with the plutonium. The second precipitation of the cycle was known as the "product precipitation" and carried only a small portion of the remaining

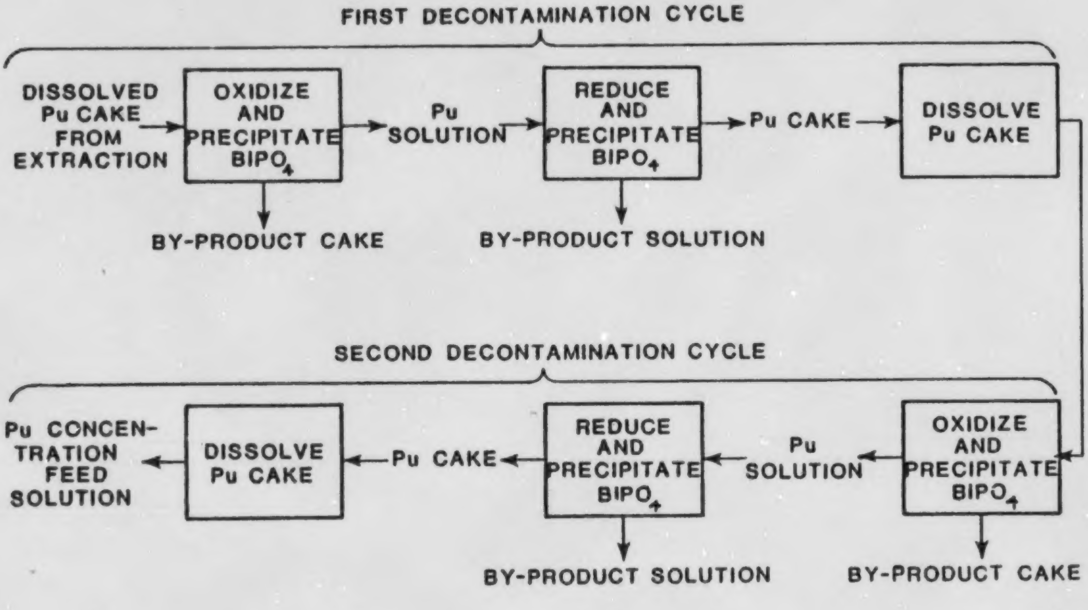
FIRST DECONTAMINATION CYCLE
DISSOLVED Pu CAKE FROM EXTRACTION
OXIDIZE AND PRECIPITATE BIPO4
Pu SOLUTION
REDUCE AND PRECIPITATE BIPO4
Pu CAKE
DISSOLVE Pu CAKE
BY-PRODUCT CAKE
BY-PRODUCT SOLUTION
SECOND DECONTAMINATION CYCLE
Pu CONCENTRATION FEED SOLUTION
DISSOLVE Pu CAKE
Pu CAKE
REDUCE AND PRECIPITATE BIPO4
Pu SOLUTION
OXIDIZE AND PRECIPITATE BIPO4
BY-PRODUCT SOLUTION
BY-PRODUCT CAKE

Figure 23-4-9. Decontamination cycles.

fission products along with the reduced plutonium. In the first decontamination cycle, the efficiency of fission-product removal in the by-product precipitate was increased by precipitation of zirconium and ceric phosphate scavengers in addition to bismuth phosphate. The degree to which fission products were carried in the product precipitate was decreased by the addition of bismuth phosphate in the presence of SiF_6^{-2}, which solubilized the phosphate-insoluble fission products.

The second decontamination cycle was the same as the first, except that no cerium or zirconium scavengers were added. In the decontamination cycles, the plutonium was oxidized by sodium bismuthate ($NaBiO_3$) in a nitric acid solution of bismuth phosphate. The hexavalent plutonium in the form of Pu_2^{+2} was reduced to Pu^{+4} after the by-product precipitation when the solution was heated after the addition of ferrous ammonium sulfate. The introduction of Fe^{+3} in this manner also aided in the decontamination by reducing the carrying of rare-earth fission products on the bismuth phosphate precipitate. In the by-product step of the first cycle, the loss of plutonium to the by-product cake was increased by scavengers. This is largely due to the increased cake size; its inability to be washed as effectively. Zirconium phosphate is a gelatinous, bulky precipitate difficult to centrifuge. However, when coprecipitated with ceric phosphate, it becomes sufficiently cemented to be easily centrifuged.

In order to reduce the volume of plutonium product to make the concentration step of the process simpler, the plutonium was carried on successively smaller quantities of bismuth phosphate in the two decontamination cycles. This was accomplished by a reduction of the concentration of bismuth in the product solution. The standard equipment group was used in both cycles.

CONCENTRATION PROCESS

After the decontamination cycles, the plutonium product had been decontaminated by a factor of about 3 x 10^5. Prior to performance of the isolation stage, an additional decontamination of about 33 was needed. This additional decontamination was accomplished in the concentration (Figure 23-4-10). In the concentration stage, the plutonium product was concentrated to the point, with respect to solution volume and amount of associated carrier, that it could be directly precipitated without carrier in the isolation stage. After leaving the concentration stage, the plutonium product

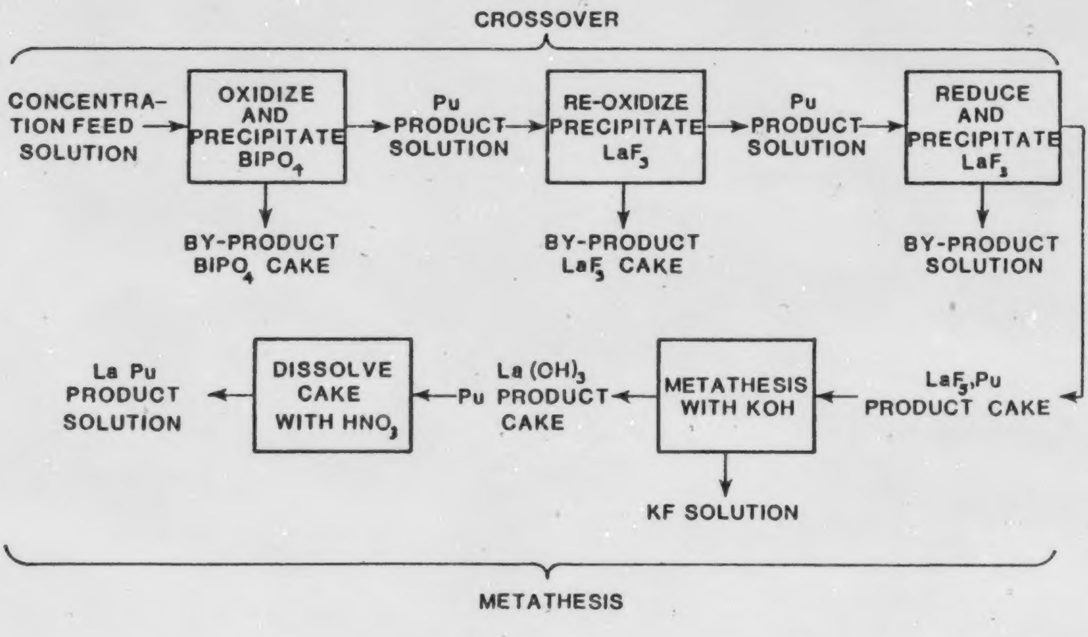
CROSSOVER
CONCENTRATION FEED SOLUTION
OXIDIZE AND PRECIPITATE BIPO4
Pu PRODUCT SOLUTION
RE-OXIDIZE PRECIPITATE LaF3
Pu PRODUCT SOLUTION
REDUCE AND PRECIPITATE LaF3
BY-PRODUCT BIPO4 CAKE
BY-PRODUCT LaF3 CAKE
BY-PRODUCT SOLUTION
La Pu PRODUCT SOLUTION
DISSOLVE CAKE WITH HNO3
Pu
La (OH)3 PRODUCT CAKE
METATHESIS WITH KOH
LaF3,Pu PRODUCT CAKE
KF SOLUTION
METATHESIS

Figure 23-4-10. The concentration stage.

solution could be handled in the isolation stage with no shielding at a small distance with no radiation hazard.

To carry out the objectives of concentration and further decontamination, it was necessary to –

- Supplement removal of two major fission products – zirconium and columbium – already almost eliminated in the previous stages.
- Eliminate remaining fission products, lanthanum, and rare earth components as completely as possible.
- Separate the bismuth phosphate carrier from the plutonium and crossover to a carrier that would carry the plutonium at a lower carrier-to-product weight ration; for example, lanthanum fluoride.
- Convert the relatively acid-insoluble LaF_3 plutonium precipitate to a highly soluble compound such as lanthanum hydroxide to deliver a small-volume concentrated solution.

The bismuth phosphate plutonium solution from the second decontamination cycle had a fission-product gamma activity that was essentially 25% lanthanum and 75% zirconium and columbium.

The first step of the stage consisted of oxidation and bismuth phosphate by-product removal without scavengers. This step served to eliminate the bismuth carrier and most of the zirconium and columbium fission products. A supplementary permanganate oxidation of the plutonium solution then was performed to ensure that the plutonium was maintained in its hexavalent state. Then a lanthanum fluoride by-product precipitation was carried out, and most of the lanthanum and rare-earth fission products were removed since they are fluoride insoluble. The plutonium product solution was now ready for crossover to another carrier, lanthanum.

The plutonium solution was reduced with oxalic acid catalyzed with Mn^{+2} ions from the permanganate, and a lanthanum fluoride product precipitation was carried out. Because of difficulty in the separation of lanthanum fluoride precipitates, which are almost colloidal in nature, the first centrifuge was returned to the precipitator and the process repeated. Very little further decontamination was accomplished in the phase, as most of the remaining fission products were fluoride insoluble.

The plutonium product now had been separated with a relatively small weight of carrier. Since the carrier was only slightly soluble in acid, the lanthanum fluoride plutonium precipitate was converted, or metathesized, to a lanthanum hydroxide product by digestion with a potassium hydroxide ($La[OH]_3$) precipitate by centrifugation, and was slurried back into a wash solution to dilute the fluoride ions liberated by metathesis. The wash solution was high enough in potassium hydroxide to prevent colloidal dispersion of the lanthanum hydroxide in the second centrifugation. The fluoride ions had to be removed in order that when the lanthanum hydroxide precipitate was dissolved in acid, reprecipitation of lanthanum fluoride did not occur. The final step of the concentration stage was to dissolve the entire precipitate cake in nitric acid to produce a small-volume plutonium product solution of $La(NO_3)_3$-$Pu(NO_3)_4$ for the isolation stage of the process.

ISOLATION PROCESS

In all the previous stages, plutonium was not identified in any way as a pure compound, but, rather, as being associated with large amounts of carriers. The final plutonium solution from the concentration process was delivered to the isolation stage in a rather small volume of solution per batch of fuel being processed. The isolation stage was performed to separate the plutonium from the carrier and to prepare a final product of plutonium salt having a minimum purity of 90%. The separation of plutonium from the lanthanum and other ions involved a direct precipitation of a plutonium compound for the first in the process. To obtain the desired separation from impurities and carrier, a plutonium compound that met certain conditions was selected:

- Have a low solubility in the precipitation medium.
- Must be easily separated from the solution mechanically.
- Must be able to be purified from other cations such as La, Fe, and Zr already obtained.
- Must be easily dissolved.

Of the known plutonium compounds, plutonium peroxide most closely met the conditions. It exhibited a low solubility in the reaction medium that was used, was easily redissolved with nitric acid to give nitrate, and could be separated easily by filtration from the solution. Additional precipitation of plutonium peroxide yielded a high purification from the other cations since they would not precipitate as peroxides, nor would they be carried appreciably by plutonium peroxide.

The isolation stage is diagrammed in Figure 23-4-11. The plutonium solution from the concentration process was filtered upon entering the first cycle of the isolation process. Separation of various insoluble materials was the purpose of this filtration. As received from the con-

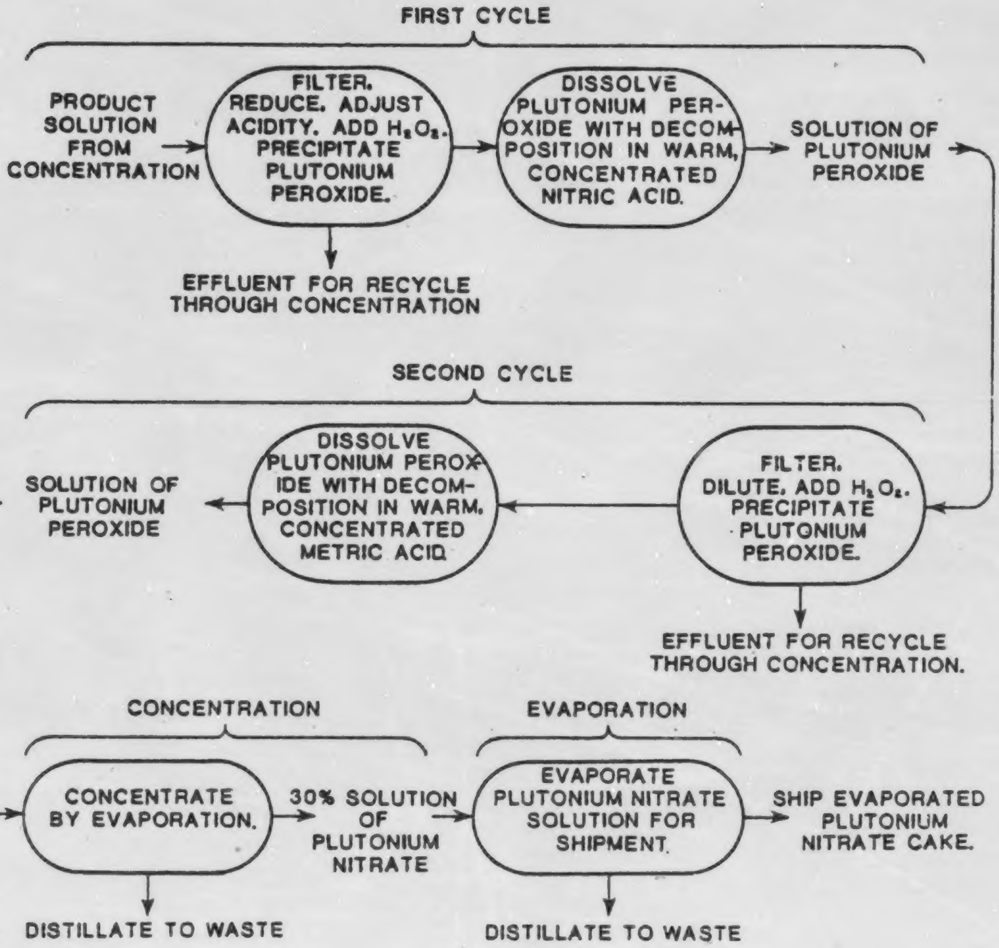
FIRST CYCLE
PRODUCT SOLUTION FROM CONCENTRATION
FILTER. REDUCE. ADJUST ACIDITY. ADD H₂O₂. PRECIPITATE PLUTONIUM PEROXIDE.
DISSOLVE PLUTONIUM PEROXIDE WITH DECOMPOSITION IN WARM, CONCENTRATED NITRIC ACID.
SOLUTION OF PLUTONIUM PEROXIDE
EFFLUENT FOR RECYCLE THROUGH CONCENTRATION
SECOND CYCLE
FILTER. DILUTE. ADD H₂O₂. PRECIPITATE PLUTONIUM PEROXIDE.
DISSOLVE PLUTONIUM PEROXIDE WITH DECOMPOSITION IN WARM, CONCENTRATED METRIC ACID.
SOLUTION OF PLUTONIUM PEROXIDE
EFFLUENT FOR RECYCLE THROUGH CONCENTRATION.
CONCENTRATION
CONCENTRATE BY EVAPORATION.
30% SOLUTION OF PLUTONIUM NITRATE
DISTILLATE TO WASTE
EVAPORATION
EVAPORATE PLUTONIUM NITRATE SOLUTION FOR SHIPMENT.
SHIP EVAPORATED PLUTONIUM NITRATE CAKE.
DISTILLATE TO WASTE

Figure 23-4-11. The isolation process.

centration process, a large portion of the plutonium present was in the oxidized form as hexavalent plutonium. Hexavalent plutonium does not precipitate with hydrogen peroxide (H_2O_2); and since hydrogen peroxide will reduce it very slowly, the reduction of hexavalent to tetravalent or trivalent plutonium was required before the hydrogen peroxide could be added. Any trivalent plutonium formed in the reduction process was of no practical consequence since it was rapidly reoxidized to tetravalent in the presence of hydrogen peroxide. Prereduction of the solution in the first cycle, therefore, was carried out by use of ammonium sulfite in the presence of ammonium sulfate. Precipitation of the plutonium peroxide was performed by the addition of the hydrogen peroxide after the acidity had been set to produce a precipitate with low solubility and fast settling characteristics. After a settling period, the solution was decanted, leaving some residual solution, called a "heel," over the cake. The precipitate then was washed three times with sulfuric acid and agitated. All the wash solutions also were decanted and combined with the original solution in the catch tank. Such solutions again were run through the concentration stage. The precipitate of plutonium peroxide then was dissolved in nitric acid.

In the second cycle, the solution from the first cycle was filtered again to remove small quantities of insoluble materials. The filtered solution was transferred to the second precipitator. A plutonium purity of approximately 80% was obtained in the first cycle. The purpose of the second cycle was to obtain an even higher purity. The solution was diluted with water to obtain a lower nitric acid normality. Sulfuric acid then was added to the solution, and the hydrogen peroxide concentration was adjusted. Ammonium sulfate was not used since an insoluble salt of plutonium was observed to precipitate in the adjusting tank later in the isolation process if it was used. Washes were performed in much the same manner as in the first cycle. The plutonium peroxide precipitate again was dissolved in nitric acid.

Water and nitric acid were distilled from the solution in a still. Some plutonium solution remained as a heel in the still. The distilled solution was transferred to an adjustment tank, where it was sampled for concentration and purity. The plutonium solution in the adjustment tank was delivered in appropriate portions of plutonium to a weight tank, at which point in time the weight of solution delivered to a sample can could be measured. The contents of the can were evaporated further by heating of the can in a glycerine bath. The evaporation was continued until the weight of the distillate collected indicated that a certain amount of material remained in the sample can. After cooling, the material in the sample can appeared to be a glassy plastic mass, which was considered safe for shipment.

The waste solutions left from the first and second cycles of the isolation stage had appreciable quantities of plutonium present and, therefore, were returned for another pass in the concentration stage. The transportation of these solutions to the concentration building represented a possible health hazard due to the composition of hydrogen peroxide. For this reason, among others, the hydrogen peroxide was decomposed in the isolation building. Sodium nitrite ($NaNO_2$) was added to the hydrogen peroxide solution to form $NaNO_3$ and water.

The isolation process equipment requirements were simpler than those for the previous stages in the process. Since the radiation level was very low, direct visual control of the isolation stage was employed. Because of the toxicity of plutonium, the primary hazard in the isolation building was the spreading of plutonium. To avoid disperson of plutonium, all operations were carried out in closed vessels installed within a well-ventilated hood.

Since the isolation stage was the first process to have the plutonium in a highly concentrated state, the possibility of criticality became an important consideration. All process vessels were designed to incorporate neutron absorbers. The absorbers consisted of pipes, hollow agitator shafts, and discs loaded with 10% Cd – 90% Pb shot. The precipitation tank used in the isolation of the plutonium is illustrated in Figure 23-4-12. It demonstrates incorporation of the neutron absorbers into the vessel design.

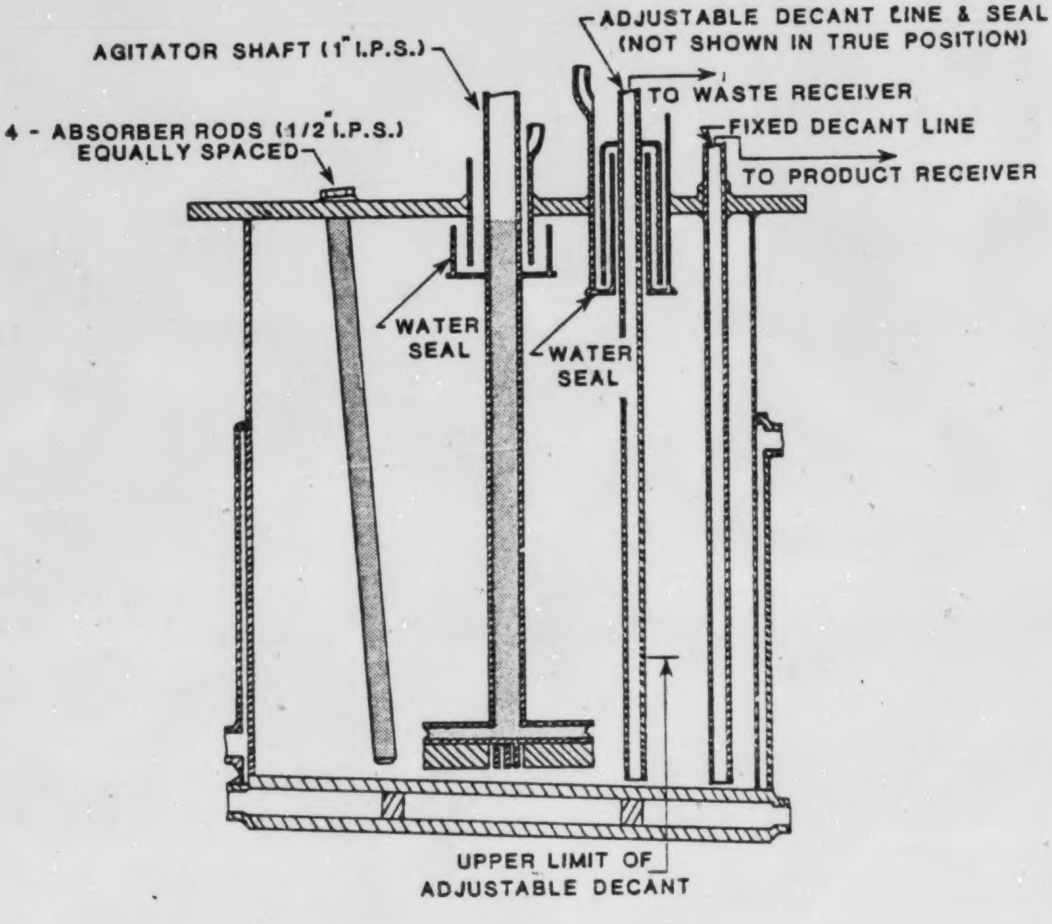
ADJUSTABLE DECANT LINE & SEAL
(NOT SHOWN IN TRUE POSITION)
AGITATOR SHAFT (1" I.P.S.)
TO WASTE RECEIVER
4 - ABSORBER RODS (1/2" I.P.S.)
EQUALLY SPACED
FIXED DECANT LINE
TO PRODUCT RECEIVER
WATER SEAL
WATER SEAL
UPPER LIMIT OF ADJUSTABLE DECANT

Figure 23-4-12. Precipitation tank.

WASTE PRODUCTS FROM THE PROCESS

The chief types of wastes from each portion of the precipitation process and their disposal are outlined below. The metal solution, extraction, and decontamination cycles of the process produced the following types of radioactive wastes:

- Coating removal waste (small but contained an undetermined amount of radiation).
- Metal waste from extraction, containing all the uranium and about 90% of the original fission-product activity.
- By-product cake solution and waste solutions from the decontamination cycles, containing a little less than 10% of the original fission product activity.

These wastes were stored in a series of buried tanks on the Hanford site.

Wastes from the concentration stage comprised less than 0.001% of the original fission product activity and about 4% of the plutonium originally in the uranium slugs. These wastes were sent underground. The wastes from the isolation stage contained very little plutonium and were jetted in a reverse-flow well, or buried pump, after neutralization of the hydrogen peroxide component with sodium hydroxide.

SAMPLING DURING THE PROCESS

Representative sampling of process solutions was of prime importance in the control of the extraction and decontamination processes. In order to obtain a representative sample, the solution to be sampled had to be agitated to ensure its uniformity. The sampling device also had to be designed to not permit concentration, dilution, or segregation of any part of the solution in the system. The sampler used at Hanford was an airlift operated in conjunction with an air jet. Its purpose was to make accessible a representative portion (about 4 ml) of the solution contained in a given tank in the heavily shielded process cells.

A sampler and associated system is depicted in Figure 23-4-13. The samplers were located in the cell walls in lead-shielded pits about two feet below the deck level. A stainless steel pipe with a special splash plate on the bottom and a lead shielded cup ran from the sampler cup to the deck, on which the personnel were allowed. This passage was used to withdraw the samples. Usually, a 0.5- to 1.0-ml portion of the sample was withdrawn from the cup and placed into a portable shield for analysis. Samples of less radioactive solutions from the plant were pipetted from the cup. The special splash plate baffled downward the fresh solution entering the cup to ensure complete flushing of the old sample solution from the cup.

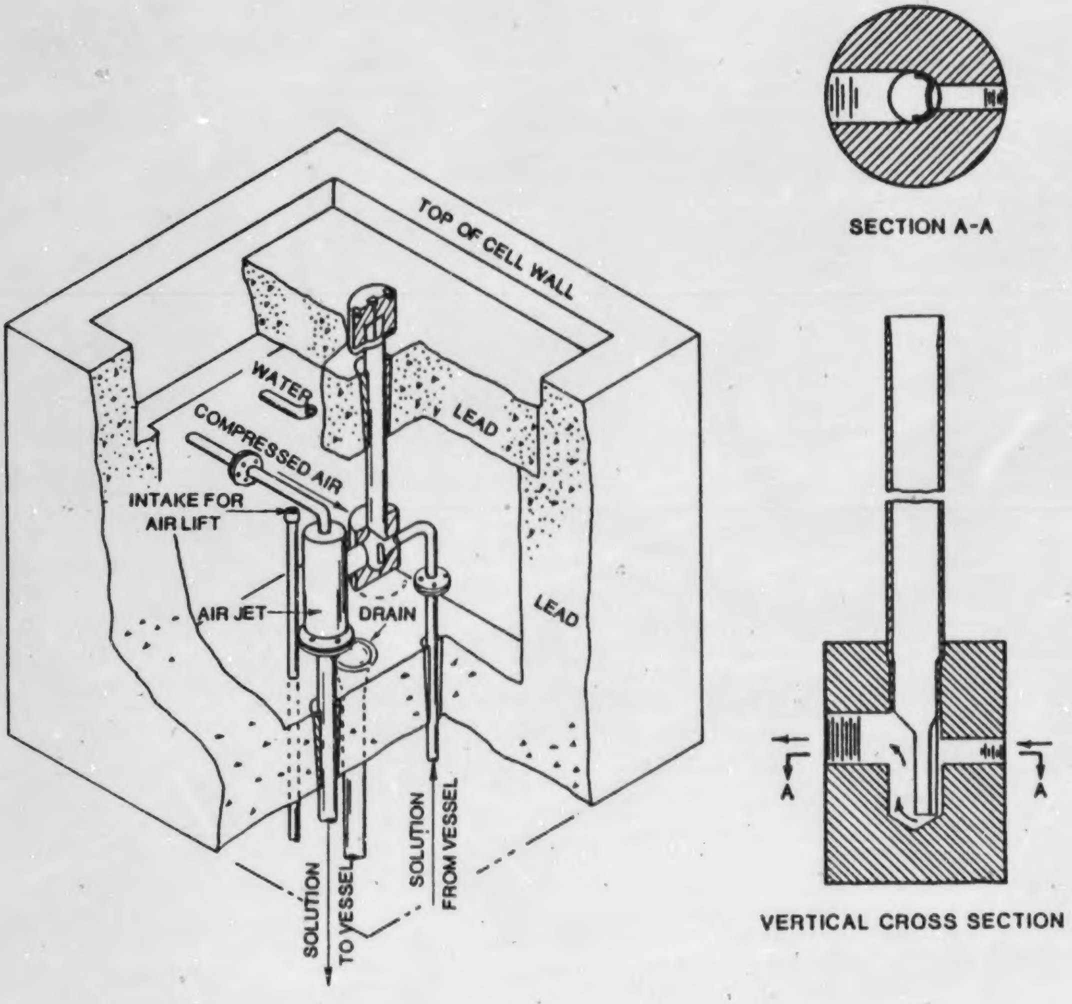
SECTION A-A
TOP OF CELL WALL
WATER
LEAD
COMPRESSED AIR
INTAKE FOR AIR LIFT
AIR JET
DRAIN
LEAD
A
A
VERTICAL CROSS SECTION
SOLUTION TO VESSEL
SOLUTION FROM VESSEL

Figure 23-4-13. Sampler.

SAFETY AND SAFETY-RELATED MONITORING

Materials handled in the extraction, decontamination, and concentration stages were radioactive to various degrees. Provision to measure the radiation intensity in those processes served two purposes: (1) Radiation levels in a process vessel gave invaluable information about the process, and (2) radiation levels in the inhabited areas gave information necessary to determine the degree of access that could be permitted. The radiation intensity information from the process cells indicated the activity of the solutions inside the tanks, permitted to operators to "observe" the solutions entering and leaving the process vessels, gave an indication of the effectiveness of the decontamination stage, and showed when it was safe for personnel to approach the cells for maintenance purposes. Stack gases were monitored to ensure adequate control of quantities of radioactive gases emitted from the plant. The cooling water discharged from the plant also was monitored continually to ensure adequate control of radioactivity levels in liquids released to the environment.

Due to the radiation hazards associated with most of the process, many remote visual and audible process monitoring aids were employed. All the centrifuges were equipped with a wobble meter to detect any imbalance in the centrifuge bowl. A magnetic pick-up device on the centrifuge modulated a 60-cycle signal, whose amplitude was proportional to the centrifuge shaft displacement. The signal was impressed on the vertical deflection plates of a cathode ray tube, and the horizontal deflection plates were connected to a 60-cycle source. The operator then would see a closed pattern, which, ideally, expanded from a straight line to an ellipse and back again. The magnitude of this fluctuation was proportional to the wobble of the centrifuge shaft.

All process tanks were equipped with contact microphones. The operator, by listening to loud speakers, could determine, to some degree, what was occurring in the tank. The operator was able to determine if the agitator worked properly and could hear solutions being loaded and unloaded. The usefulness of the microphones increased with operator experience. A departure from the overall noise characteristic of the cell indicated some mechanical problem.

Two portable periscopes also were available for inspection of the interior of the centrifuge visually. Such a periscope is depicted in Figure 23-4-14.

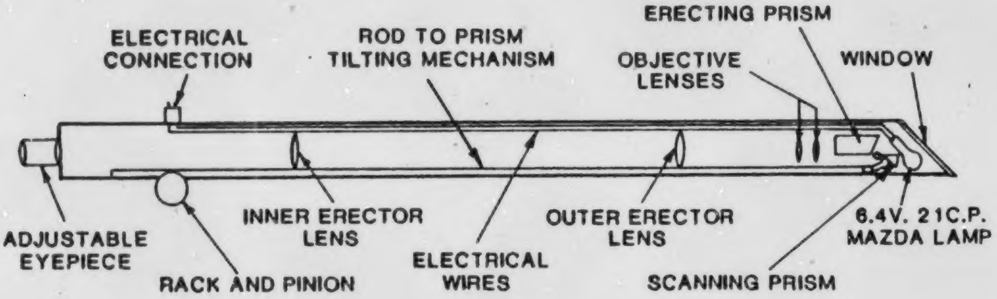
ELECTRICAL CONNECTION
ROD TO PRISM TILTING MECHANISM
ERECTING PRISM
OBJECTIVE LENSES
WINDOW
ADJUSTABLE EYEPIECE
INNER ERECTOR LENS
RACK AND PINION
ELECTRICAL WIRES
OUTER ERECTOR LENS
SCANNING PRISM
6.4V. 21C.P. MAZDA LAMP

Figure 23-4-14. Periscope for viewing inside of centrifuge.

EXERCISES

1. The precipitation process first was used as a laboratory technique to isolate plutonium. Research the exact process that was used in the laboratory, and write a brief description of the process. Note the similarities and differences between the process on the laboratory scale and on the large scale.
2. Look at the precipitation process with an eye toward improving the remote monitoring systems using state-of-the-art technology. Describe how you would monitor the different phases of the precipitation process if you were designing the plant now.

MATERIALS

FOR SOLUBILITY PROCEDURE

$AgNO_3$.
HCl.
Distilled water.
HNO_3.
H_2SO_4.
KI solution.
NaOH.
$K_2S_2O_8$.

FOR COPRECIPITATION PROCEDURE

Microcentrifuge and centrifuge tubes.
Radium-DEF solution (about 1 microcurie per ml).
Lead nitrate solution.
Bismuth nitrate solution.
10% sulfuric acid.
Sodium hydroxide solution.
10% HCl.
Carrier-free ^{32}P (about 0.1 microcurie/ml).
^{131}I (about 0.1 microcurie/ml).
Ferric chloride solution.
Ammonium hydroxide solution.
Isopropyl ether.
Well counter.
End-window GM counter.
Scintillation detector.
Graph paper.

PROCEDURES

NOTE: This section contains the following procedures: (1) "Demonstration of Solubility" and (2) Coprecipitation Phenomena." Both procedures may be performed; however, if only one is performed, the coprecipitation procedure is recommended.

DEMONSTRATION OF SOLUBILITY

Since it is impractical to use plutonium solutions and precipitates to demonstrate the process, the chemistry of silver will be used here to demonstrate solubility of salts, complex ions, and the oxidation-reduction reactions that were important to a precipitation process.

PART A

Only the +1 state of silver is of importance in aqueous solutions. The first portion of the lab will be concerned with the preparation of silver chloride.

1. To 1 ml of 0.1 M $AgNO_3$ add one or two drops ot 6 M HCl. The precipitate of AgCl is only slightly soluble and as a result, the reagent Ag^+ is useful for detecting the presence of Cl^-.
2. Treat the suspension with several ml of 6 M HCl, and agitate the mixture. Dissolution of the AgCl is due to the formation of complexes such as $AgCl_2^-$ and $AgCl_3^{-2}$.
3. Add the solution to a beaker containing about 200 ml of distilled water. Explain what occurs.
4. Add three or four drops of 6 M HCl to a mixture of 1 ml of 0.1 M $AgNO_3$ and about 3 ml of water. Centrifuge the precipitate off; wash it thoroughly with water. Transfer half the sample to a clean porcelain dish; add about 3 ml of 16 M HNO_3 and, heat the mixture just to dryness in a fume hood. Stir up the residue with several ml of water, decant the solution into a test tube, and test for presence of Ag^+.

5. Clean the porcelain dish; transfer the other half of the AgCl sample to it. Add about 3 ml of 18 M H_2SO_4; heat the mixture in a fume hood until the liquid volume has been reduced by a factor of 2 and thick white fumes appear. Allow dish to cool and cautiously add about 5 ml of water. Test again for Ag^+.
Write the equations for the reactions in step 4 and 5.

PART B

Silver forms many sparingly soluble salts such as AgCl, Ag_2SO_4, Ag_2CO_3, and Ag_2S. AgI is less soluble than AgCl; that is, a saturated solution of AgI containing 1 M I^- has a lower concentration than does a saturated solution of AgC containing a 1 M Cl^-. Thus, it is predicted that, if I^- is added to a suspension of AgCl, the white AgCl should be converted to yellow AgI.

1. Add several ml of KI solution to a suspension of AgCl prepared from 1 ml of 0.1 M $AgNO_3$. In addition, try to carry out the reverse reaction. Add several ml of NaCl solution to a suspension of AgI prepared by the addition of five drops of KI solution to 1 ml of 0.1 M $AgNO_3$. From this result the student should conclude that AgI is less soluble than AgCl.

PART C

Oxidation or reduction reactions of Pu were important in the precipitation process. The oxidation and reduction of silver serve to demonstrate some important properties of oxidation-reduction reactions.

1. Add 4 ml of 6 M NH_3 and 1 ml of 6 M NaOH to 50 ml of water. Place 2 ml of 0.1 M $AgNO_3$ into a clean test tube. Slowly add ammonia-hydroxide solution, drop by drop, until the silver oxide that initially precipitates just dissolves.
2. The resulting solution (Tollen's reagent) should not be kept longer than 10 minutes, or an explosive precipitate may be formed. The solution can be destroyed if washed down the drain with tap water.
3. Add a drop of dextrose (corn syrup) solution; allow the solution to stand for several minutes; and note the results. Pour the solution down the drain, and wash it down.
4. The silver mirror can be dissoved in nitric acid.
5. Drop a short length of clean copper wire into a test tube containing 2 ml of 0.1 M $AgNO_3$. Examine the mixture after 30 minutes or so; write the equation for the reaction. What conclusions can be reached regarding relative magnitudes of the reduction potentials of Ag^+ and Cu^{+2}.
6. Mix 1 ml each of 6 M NaOH, 0.1 M $K_2S_2O_8$, and 0.1 M $AgNO_3$ in a test tube; heat the test tube with occasional swirling in a beaker of boiling water for about 15 minutes. Collect the black precipitate of AgO by centrifugation, and wash it several times with water. Write an equation for the synthesis. The $S_2O_8^{-2}$ ion has been reduced to SO_4^{-2}. Treat one-half the sample with an acidic KI solution; heat the other half in a porcelain dish. Interpret observations.

COPRECIPITATION PHENOMENA

PART A: PRECIPITATION OF RADIUM-D (^{210}Pb) AS A SULFATE

1. To each of three test tubes that contain 1 1/2 ml of 10% nitric acid, add 100 lambdas of Ra-DEF solution. Treat each test tube as follows: (a) To tube A-1, add nothing (carrier free); (b) to tube A-2, add 3 drops of lead nitrate solution (the lead-carrier solution); and (c) to tube A-3, add 3 drops of lead nitrate solution and 3 drops of bismuth nitrate solution (the bismuth carrier solution). Record applicable data in Data Table 23-4-1.
2. To each tube, add 10 drops of 10% sulfuric acid. Mix the contents, and allow to digest for 1 hour in a hot water bath. Tubes A-2 and A-3 should contain a precipitate. Let the tubes cool, and centrifuge. Transfer 1 ml of supernatant from each tube; wash precipitates to planchets and dry them. Prevent loss of dry precipitate by applying a drop of diluted collodion. Finally, evaporate all solvents thoroughly under the infrared lamp.
3. Activity of each precipitate then is measured in a proportional counter on both the alpha and beta plateaus. Repeat the activity measurements in 1, 2, 4, and 8 days, recording all data in Data Table 23-4-1.

PART B: PRECIPITATION OF RADIUM-E (^{210}Bi) AS A BASIC SALT

1. To each of three test tubes containing 1 1/2 ml of water, add 100 lambdas of Ra-DEF solution. Treat each

as follows:

- To tube B-1, add nothing (carrier free).
- To tube B-2, add 3 drops of bismuth nitrate solution.
- To tube B-3, add 3 drops of bismuth nitrate solution and 3 drops of lead nitrate or lead acetate solution.

2. To tube B-2, add NaOH solution dropwise until no further precipitate forms. Add exactly the same amount to the other tubes. Mix, and centrifuge. Transfer 1 ml of supernatant liquid from each tube to a planchet; measure the activity of each solution with an end-window GM counter. Record all appropriate date in Data Table 23-4-2.
3. To planchet containing the supernatant solution from tube B-3, add very carefully an excess concentrated HCl to neutralize the NaOH. Dry the solution under the infrared lamp until no excess HCl remains. Measure activity of this sample each day for several days in the same manner as in Part A.
4. Complete Data Table 23-4-2.

ANALYSIS OF PRECIPITATION PROCEDURE

1. Plot activities of the samples as a function of time on linear graph paper.
2. Identify the nuclide or nuclides responsible for each observed activity curve plotted in Step 1.
3. For each precipitation conducted above, determine the fate of each component: radium D (^{210}Pb), radium E (^{210}Bi), and radium F (^{210}Po). Indicate the extent

that each was precipitated or left in the solution.

4. Explain the behavior of each component on the basis of precipitation, carriers, holdback agents, etc.

DATA TABLE 23-4-1

DATA FOR COPRECIPITATION PHENOMENA, PART A

Step A-3	Elapsed Time (Hours)	Tube (A-1 A-2, A-3)	Activity Alpha Plateau	Activity Beta Plateau	Alpha Activity	Beta Activity
	up to 8 days					

DATA TABLE 23-4-2

DATA FOR COPRECIPITATION PHENOMENA, PART B

Elapsed Time	Bkg cpm	Ra-DEF Standard	Unknown cpm	Unknown Corrected cpm

REFERENCE MATERIALS

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Seaborg and Katz. The Actinide Elements. National Nuclear Energy Series Division IV, Vol 14A (1954).

TEST

SECTION I: FILL IN THE BLANKS.

1. The precipitation technique was based upon the chemical fact that the ___________ state of plutonium is ________, while the ________ state of plutonium forms soluble compounds.
2. Since the plutonium was only present originally in trace amounts in the process solutions, it was coprecipitated by use of elements known as ____________. Other elements known as ______________ and ____________ served to keep the trace element in solution.
3. To obtain a usable purity, the associated radioactivity of the plutonium product had to be decontaminated by a factor of _______________.
4. Concrete shielding of the process vessels as well as _______________ constituted the principal means of protection of personnel from radiation hazards.
5. A precipitation in which the plutonium was precipitated was known as a ____________ precipitation, while a precipitation that left the plutonium in solution was known as a _________________ precipitation.
6. Until the isolation phase, not enough plutonium in a concentrated, pure form existed in solution to pose a _______________ hazard.

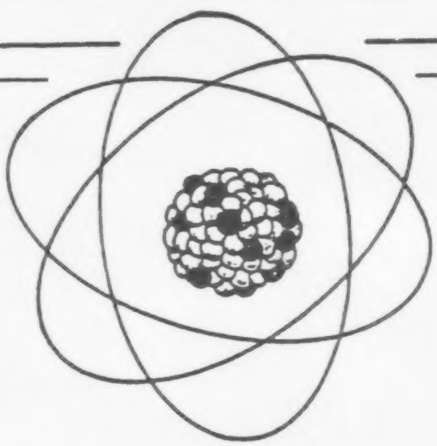
SECTION II.

7. List and describe briefly the purposes of the four phases of the precipitation process.

8. Explain why it was necessary to reduce the metal solution prior to the extraction of plutonium from the solution.

9. Compare similarities and differences between the precipitation process and solvent extraction. Comment on the fissile material losses, process complexities, and safety considerations.

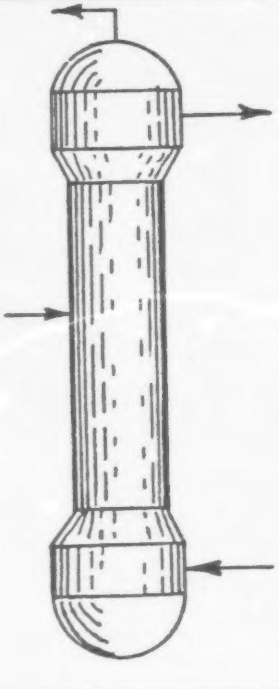
10. Discuss importance of the carry-over process. How is it accomplished?



NUCLEAR TECHNOLOGY

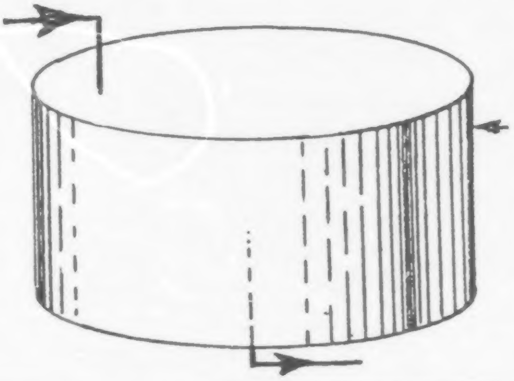
MODULE 23-5

TECHNIQUES OF CHEMICAL CONCENTRATION



NUCLEAR CHEMICAL
PROCESSES

COURSE 23



ORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
⇨ MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

The rapidity with which technology has progressed has affected major fields of science and technology profoundly. This technological evolution has stimulated the rate at which new development are applied and widened: In these days of energy consciousness and concern for supplies of natural resources, new and widespread interest has been aroused with respect to materials hitherto unknown, or, if known, regarded as little more than scientific curiosities. New demand for these materials has prompted the necessity for new techniques and processes for their development. Regrettably some of these materials are not naturally abundant.

Some radioactive materials are produced and may pose a hazard, not only to living organisms, but, as well, to entire ecological systems. With either scarce resources or dangerously radioactive materials, there is a need to concentrate different substances for use in industry or for permanent disposal, as in the case of many nuclear waste products.

It will be the objective of this module to describe –

- Different techniques of concentration.
- Nature of chemicals to be concentrated.
- Concentration equipment.
- Instrumentation and monitoring of the concentration process.
- Process procedures and specifications.
- Safety practices and process forms.
- Safety measures commonly employed in the processes.

Among the materials not readily abundant in nature are the rare earth metals. The electronic industry demands rare metals for transistors and semiconductors, photoelectric cells and rectifiers, X-ray tubes, transmitting tubes, and capacitors. Due to the limited availability of rare earth materials, concentration techniques have been developed to aid in rare earth recovery.

Radioactive materials such as fission products (many of which are rare earths) play important roles in the recovery of uranium and plutonium from spent fuel elements. Indeed the entire transuranium process is a matter of various concentration steps. Radioactive gases as well as solids are concentrated in the nuclear industry.

Clearly, a need exists for a close examination of concentration techniques, not only for work within the nuclear industry, but also with regard to natural resource exploitation, allocation, and use.

MODULE PREREQUISITES

The student should have completed Course 1, "Radiation Physics"; Course 2, "Radiation Protection I"; and from Course 23, Modules 23-2, "Ion Exchange"; 23-3, "Solvent Extraction;" and 23-4, "Precipitation Techniques and Centrifugation." In particular the student should have some knowledge of (1) the structure and employment of the periodic table; (2) fission products and the actinides; (3) anion and cation exchange; (4) determination of resin capacity; (5) principles of selection of dilution chemicals; and (6) solvent extractions.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Explain the purpose of, and necessity for, concentration techniques.
2. Describe at least four different concentration techniques discussed in this module.
3. Describe the equipment used for chemical concentrations.
4. Describe the instrumentation and monitoring of the concentration process.
5. Explain the purpose of process procedures and process specifications.
6. Explain the reason for the substitution of nonradioactive chemical for radioactive materials in concentration models.

Chemical concentration is not an entity unto itself: It almost invariably is performed in conjunction with other chemical processes.

The very word "concentration" means "to compact, consolidate, collect, or purify." Technicians concentrate a chemical or element by increasing its molarity, by removing some other substance from it, or by making it insoluble. Other techniques include concentration by maintaining a substance in solution and making its contaminant insoluble. Purification of anything is a form of concentration.

In the nuclear industry alone, there are concentration procedures that can process thousands of gallons of solution to produce a radioisotope for medical therapy or a tracer in agricultural use or to recover plutonium from spent fuel elements.

The predominant purpose of chemical processing of irradiated nuclear reactor materials is the recovery and purification of fissile constituents.

Radioisotope preparations must be of high radiochemical purity and free from inactive chemical impurities. The products usually are shipped in solution, and it is desirable to keep the volume at the lowest practical level to minimize the amount of shielding required for shipping. In most cases, less than a milligram of radiochemical is processed, and presence of the material cannot be determined readily except by detection of its radiations. Ordinary chemical methods find limited use in radioisotope production; specialized techniques are required.

The design of a radiochemical process probably must take into account the feasibility of the operations to a greater extent than any other type of chemical design. A small change in the chemistry can save thousands of dollars worth of time and equipment, simply because some remote chemical operations can be performed more easily than others.

Many different techniques are utilized for the purposes of concentration. This module will discuss six of the more common methods (listed below). Each will be discussed as a separate topic.

Concentration by:

- Precipitation.
- Distillation.
- Ion exchange.
- Solvent extraction.
- Crystallization and adsorption of radiocolloids.
- Concentration of a gas.

PRECIPITATION

The classical method of separating (concentrating) microgram amounts of metals from the major biological elements (sodium, potassium, and calcium) is by precipitation. Precipitation occurs when a solid is produced from solution as the result of a chemical action. The solid is called a "precipitate." This chemical change occurs in two steps — nucleation and crystal growth.

Nucleation is the process of formation within a supersaturated solution of the smallest particles capable of growth to larger particles. Crystal growth consists of deposition of materials, probably by adsorption, from solution into nuclei and particles already formed.

Contamination of a precipitate by a normally soluble material is referred to as "coprecipitation." Coprecipitation allows microgram quantities of certain elements to be precipitated by adsorption (the attraction of solute particles to a surface). Adsorption occurs when elements that make compounds crystallize in the same system can be brought down together. For example, ruthenium is coprecpitated from solution by platinum sulfide: the ruthenium sulfide is included in the platinum sulfide crystal.

A similar procedure, in which micro-amounts of a radioisotope are included in crystals, is employed. For example, cesium alum is included in crystals separated from a saturated solution of ammonium alum containing micro-amounts of cesium.

Precipitations are difficult to manage by remote control and, therefore, are limited in terms of the degree of radioactivity displayed by the precipitates. Other methods are more effective in the concentration of substances that have extremely small sensitivities (amounts of rare earth, etc., measured im millimicrograms).

Precipitation often is used for the concentration of a chemical for ion-exchange feed and as a feed preparation for solvent extractions. It is an integral part of these particular processes and is not used often as a concentration technique in and by itself.

DISTILLATION

Distillation techniques operate on the principle that different elements and compounds have different boiling points. The process is carried out in a column in which heat is applied to a particular chemical feedstock to produce vapor gases. As the vapors drift up the column, they condense out at different locations due to the temperature differences in the column. The more volatile substances (those that evaporate at lower temperatures) do not condense out until they are near the top. Before all the substances condense, the desired vapors are contained, then cooled and collected in the form of a liquid. Various components of a particular substance are separated by collection of each vapor, in turn, as it condenses.

The separation and purification of ^{131}I is a good example of the distillation process. Fission product iodine is formed within the uranium slugs during irradiation, and the general problem is to release the iodine, trap it in a suitable medium, reduce the volume, and purify it by chemical processing. After dissolution of the metal in nitric acid, iodine is distilled out, by steam air, as elemental iodine. It is partially removed from the vapor stream by absorption of the gaseous molecule into the weak nitric acid condensate, and the balance is taken out in an alkaline scrubber. The nitric-nitrous acid distillate is treated with hydrogen peroxide to oxidize nitrous acid to nitric acid, and iodine is distilled out. Dilute solutions of nitric acid have a very low intric acid vapor pressure. Distillation results in a small volume of distillate that contains very little nitric acid, but most of the iodine. The contents of the alkaline scrubber are treated in the same way after acidification with nitric acid. This crude iodine distillate, after an additional distillation, is trapped in dilute sodium for final purification in glass equipment. Purification is accomplished by oxidation of the iodine to iodate in 20% sulfuric acid-potassium permanganate solution, after which traces of nitric acid, or other volatile substances, are distilled off while the nonvolatile iodate remains in the distillate as a reducing agent. The solution volume then is adjusted; the solution is filtered; and the iodine preparation is transferred to a shielded container for storage.

ION EXCHANGE

Ion exchange frequently is used in conjunction with solvent-extraction techniques to effect concentration and additional decontamination of uranium and plutonium. Ion exchange is a reversible exchange of ions between a solid and a liquid, in which there is no substnatial changed in the physical structure (appearance) of the solid. The fission products commonly subjected to the ion-exchange process are cesium-137, strontium-90, and plutonium-238 and 239.

In treatment of nuclear waste, the "solid" is the ion-exchange material, a resin particle. A resin is a high-molecular-weight polymer that contains particular ionic groupings as a basic part of its structure. (A polymer is a compound of large molecules formed by the repetitious union of many small molecules.)

The two general types of ion-exchange resins in use today are cation resins (acidic) and anion resins (basic). Cation resins contain phenolic, sulfonic, carboxylic, or phosphoric acid groups with equal amounts of mobile (removable) ions or sodium or hydrogen ions. Anion exchangers contain amine groups attached to mobil ions such as chloride or hydroxyl ions. The mobile ions on both the anion and cation resins are exchanged for other ions of the same sign (electrical charge) in the waste material. The extent to which the exchange takes place is limited by selectivity of the resin.

A modification of the structure of the resin, known as "cross-linkage," varies it chemical/physical properties. Cross-linkage binds a linear polymer chain in the resin with another substance that produces a three dimensional insoluble copolymer. The extent of cross-linkage is indicated by an X following the name of the particular resin; for example, Dowex 50-X8.

By use of both a cation and an anion resin, it is possible to deionize a solution almost totally. The resins also may be mixed together to form a mixed bed.

As ionization proceeds, the upper layers of the resin column are complete converted to the form containing the ions in the waste solution. The location of exchange eventually will reach the bottom of the column, and exchanging ions in the waste solution will show in the effluent. This is known as "breakthrough." The process usually is discontinued before breakthrough, and the column is regenerated by reversal of the exchange process.

Most applications of ion-exchange resins to the treatment of reactor wastes involve activity levels at which the effect of radiation upon the resin is very slight. Adsorption is affected by differing amounts in regard to commercially-available resins when higher levels of radioactivity are involved.

The processes involved in radionuclide production are of an intermediate nature, in terms of size: The resin columns and associated equipment are physically small, but complicated by the presence of up to 100 curies of radionuclides, frequently emitters of gamma radiation. The radiation conditions require the use of heavy shielding, remote-control apparatus, indirect vision, and other inconvenient deterrents to operation.

In many cases, the equipment can be operated remotely; that is, entirely by pressure or vacuum, which is very desirable. Radioactive solutions are transferred to a head tank by vacuum, and the solution usually is filtered during this operation. The head tank is equipped to receive chemical reagents. The solution is passed through the column, with flow rate controlled by either the height of liquid in the head tank or pressure-vacuum control in a closed system. Effluent usually passes out through a leveling leg, which may be adjustable in order that various heights of resin beds can be used in the same column to ensure that the resin bed will remain covered with liquid at all times. The effluent is monitored constantly by a flow-type radioactivity recorder, in order that the efficiency of absorption of activity is known at all times. If proper conditions of concentration, pH, and flow rate are maintained, the cations, including the radioactive species, are taken up on the top part of the resin column. It is possible to measure the width of the band with a suitable radioactivity probe. For good results, the activity should be taken up on the top 1-to-10 percent of the column length. After thorough washing, the eluting solutions are passed through the column, and a "chromatographic" type of separation takes place as the top band is slowly broken up into further discrete bands of material, which then move in orderly fashion down the column until they appear sequentially in the effluent. The bands may be followed down the column with the radioactivity probe and progress plotted as a control measure. When the bands of activity appear in the effluent (as shown by the radiation meter chart), the product is diverted into containers for storage. At least three "cuts" are taken – one on each side of the activity band

and one in the middle at the greatest height of the peak. The middle cut usually contains the purest material.

The technician also can take up materials from solution merely by allowing a minimum quantity of ion-exchange resin to remain in suspension in the solution for a period of time. After equilibrium conditions have been attained, the liquid is filtered off; and the resin is washed, slurried in water, and transferred to the top of an uncontaminated resin bed in a column.

Eluting agents complex the various ions taken up by the resin, such as citrate ion for the separation of rare earths. The degree to which complexing occurs is controlled by the hydrogen ion concentration; and this property, together with variations among elements in their tendency to form complexes, enables chemical separations to be made.

Users of radioisotopes many times prefer to receive the radioactive materials in pure water solution or weak hydrochloric acid, which readily may be removed by evaporation. The ion-exchange column is used here to destroy the complexing action of the eluting agent by increasing the hydrogen ion concentration in the case of citrates. Simple dilution with water is performed in other cases, so that the product solution may be replaced on a very small ion-exchange column and then removed in a small volume of hydrochloric acid.

A flow diagram for fission product separation is shown in Figure 23-5-1.

Material at the start of the cycle depicted above consists of a 6N hydrochloric acid solution containing a few milligrams of mixed fission products and various cationic impurities such as Ca, Mg, Fe, Ni, Cr, Mn, Na, K, and organic matter. The solution is evaporated to near dryness and

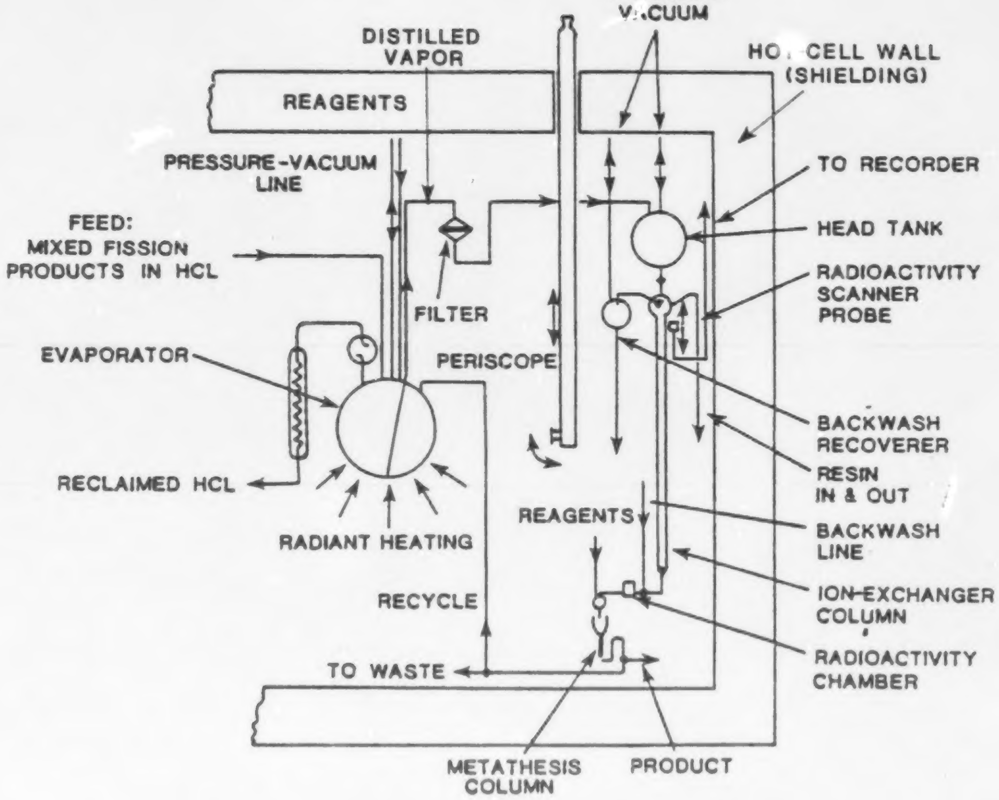

PRESSURE
VACUUM
DISTILLED
VAPOR
HOT CELL WALL
(SHIELDING)
REAGENTS
PRESSURE-VACUUM
LINE
TO RECORDER
FEED:
MIXED FISSION
PRODUCTS IN HCL
HEAD TANK
RADIOACTIVITY
SCANNER
PROBE
FILTER
EVAPORATOR
PERISCOPE
BACKWASH
RECOVERER
RESIN
IN & OUT
RECLAIMED HCL
REAGENTS
BACKWASH
LINE
RADIANT HEATING
ION-EXCHANGER
COLUMN
RECYCLE
RADIOACTIVITY
CHAMBER
TO WASTE
METATHESIS
COLUMN
PRODUCT

Figure 23-5-1. Flow sheet for fission product separation.

treated with successive portions of hot concentrated nitric acid and concentrated hydrochloric acid until all organic matter is destroyed. The solution then is heated until dry and then is redissolved as a concentrate of acid in water. It is desirable to keep the acid concentration and solution volume small at this point in order to deposit the activity in a tight band at the top of the ion-exchange column. However, if too little acid (or water) is used, losses of product by adsorption on the glass will be very high. The solution is filtered and added very slowly to an ion-exchange column (0.5 inch in diameter and approximately 50 inches long) containing a bed of 60- to 80-mesh resin. After fission products are absorbed, the column is washed thoroughly with water. Five percent citric acid solution, whose pH has been adjusted with ammonium hydroxide, then is passed through the column at a rate of one column volume per hour. The term "column volume" as used here denotes the gross apparent volume of the resin bed. Starting pH varies, depending upon the type of resin used, the rate of removal and purity desired in the various fission product bands. A typical starting pH is 2.75. The effluent passes through the apparatus for measuring intensities of the beta and gamma radiation, which are plotted automatically by electronic equipment. The bands of activity also are located by the scanning probe as they flow away from the top of the column, and a record is kept of their progress down the column. By noting the behavior of the activity bands (such as spreading, or moving too slow or too fast), the technician can exercise rather precise control, regulating flow rate and influent composition. As the bands of activity reach the base of the column, the activity of the effluent rises rapidly to a peak, or plateau, and then recedes sharply as the activity band is removed. Experience has shown just which radioelements are to be expected in each band; the ratio between beta and gamma activities in the effluent often gives evidence of the presence of the elements. The more abundant fission products are removed in the following order, as the pH of the citrate effluent is increased: Y, Eu, Sm, Pm, Nd, Pr, Ce, La, Sr, Ba.

THE RARE EARTH METALS

Fifteen rare earth elements compose Group III of the periodic table and have atomic numbers ranging from 57 to 71 inclusive. A list of the rare earth metals is depicted in Table 23-5-1.

TABLE 23-5-1
THE RARE EARTHS AND YTTRIUM

Element	Atomic Number	Atomic Weight	Valences	Oxide (Ignited in Air)	
Lanthanum	57	138.92	3	La_2O_3	Cerium group
Cerium	58	140.13	3, 4	CeO_2	
Praseodymium	59	140.92	3, 4	Pr_6O_{11}	
Neodymium	60	144.27	3	Nd_2O_3	
Promethium	61	145.	3	Pm_2O_3	
Samarium	62	150.43	2, 3	Sm_2O_3	
Europium	63	152.0	2, 3	Eu_2O_3	Terbium group
Gadolinium	64	156.9	3	Gd_2O_3	
Terbium	65	159.2	3, 4	Tb_4O_7	
Dysprosium	66	162.46	3	Dy_2O_3	
Holmium	67	164.94	3	Ho_2O_3	Yttrium group
Erbium	68	167.2	3	Er_2O_3	
Thulium	69	169.4	3	Tm_2O_3	
Ytterbium	70	173.04	2, 3	Yb_2O_3	
Lutetium	71	174.99	3	Lu_2O_3	
Yttrium	39	88.92	3	Y_2O_3	

Table 23-5-1 lists the rare earth elements and yttrium with their typical valences and oxides and their classical distribution into "cerium," "terbium," and "yttrium" groups. Yttrium in its properties usually occupies a position between dysprosium and holmium.

In addition to this specific group of elements, other metals often need to be concentrated due to a natural scarcity or relatively low concentration of accessible deposits. The handling and processing of huge amounts of worthless material are required to extract even small quantities of the desired element in either compound or elemental form.

The nuclear industry has created a need for metals of specific properties to serve as —

- Heat transfer media.
- Corrosion-resistant material and material for low neutron absorption.

SOLVENT EXTRACTION

Solvent extraction is a process that employs solvents to dissolve radionuclides to permit decontamination and recovery. These processes, for the most part, utilize methyl isobutyl ketone and tributyl phosphate as solvents. Large-scale use of solvent extraction techniques in this uranium fuel cycle usually is concerned with the recovery of plutonium from reactor material.

The basic chemistry of the extraction process depends upon the solubility of uranyl nitrate in such compounds as diethyl ether, tributyl phosphate, and other organic ethers, ketones, and alcohols. Because of this property, uranium is dissolved in aqueous solution as uranyl nitrate can be extracted from water if the solution is contacted with a water-insoluble second phase containing one of these organic solvents. Another nitrate salt, such as ammonium nitrate, added to the water phase acts as a "salting agent" and enhances the extraction. The nitrates of impure metals and fission products usually are of low solubility in the organic phase and remain in the water phase. The two phases can be separated mechanically, and the uranium can be removed from the organic phase by recontacting with water.

In applying the solubility property of uranyl nitrate to the decontamination and recovery of a uranium fuel containing fission products and plutonium, the uranium fuel first is dissolved in nitric acid. The complicating effect of corrosion-resistant cladding on the uranium will be neglected for the moment. The resulting solution is adjusted with regard to concentration of the uranium and valence state of the plutonium. A salting agent to enhance uranium extraction normally is added. The feed solution is extracted with an organic solvent such as one of the ones mentioned above; for example, with tributyl phosphate (TBP).

The uranium and plutonium are extracted quantitatively into the TBP, along with small quantities of fission products. The bulk of the fission products remains in the water phase and becomes a waste stream. The organic phase is run through a "scrub" solution for additional decontamination prior to the step in which the plutonium selectively is stripped into water by reducing it to an organic-phase, insoluble-valence state. The plutonium containing solution is subjected to further purification. A TBP scrub stream prevent simultaneous stripping of the uranium. In the final step, the uranium is stripped by differential counter-current contact of the organic stream with water. The stripped solvent is sent to a solvent recovery step for eventual reuse. The uranium solution, which has been decontaminated by a factor of approximately 10^4 from radioactive fission products, can be concentrated again and recycled for additional decontamination. Figure 23-5-2 briefly outlines the process.

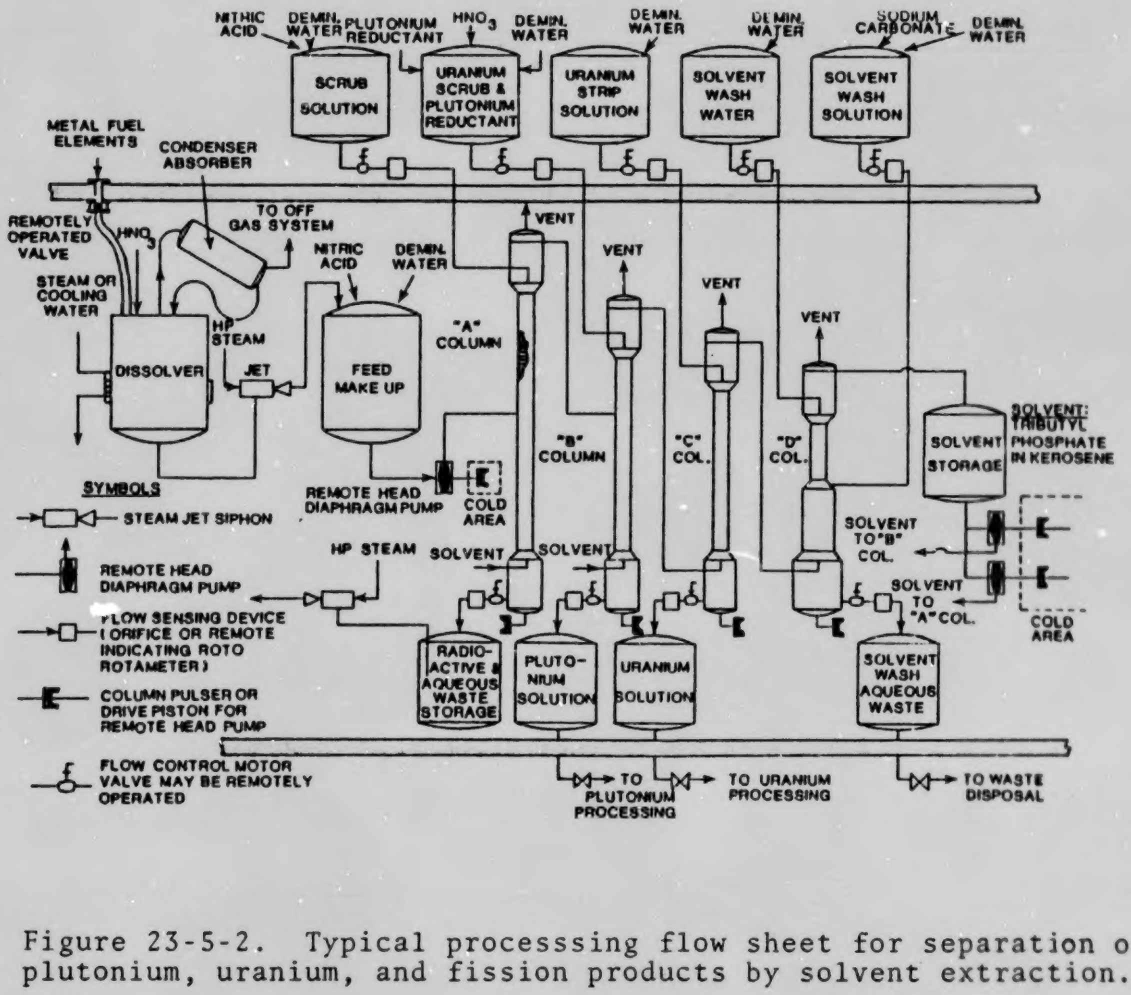

NITHIC ACID
DEMIN. WATER
PLUTONIUM REDUCTANT
HNO3
DEMIN. WATER
DEMIN. WATER
DEMIN. WATER
SODIUM CARBONATE
DEMIN. WATER
SCRUB SOLUTION
URANIUM SCRUB & PLUTONIUM REDUCTANT
URANIUM STRIP SOLUTION
SOLVENT WASH WATER
SOLVENT WASH SOLUTION
METAL FUEL ELEMENTS
CONDENSER ABSORBER
REMOTELY OPERATED VALVE
HNO3
TO OFF GAS SYSTEM
VENT
STEAM OR COOLING WATER
NITRIC ACID
DEMIN. WATER
VENT
VENT
VENT
HP STEAM
"A" COLUMN
DISSOLVER
JET
FEED MAKE UP
"B" COLUMN
"C" COL.
"D" COL.
SOLVENT STORAGE
SOLVENT: TRIBUTYL PHOSPHATE IN KEROSENE
SYMBOLS
REMOTE HEAD DIAPHRAGM PUMP
COLD AREA
STEAM JET SIPHON
SOLVENT TO "B" COL.
HP STEAM
SOLVENT
SOLVENT
REMOTE HEAD DIAPHRAGM PUMP
SOLVENT TO "A" COL.
COLD AREA
FLOW SENSING DEVICE (ORIFICE OR REMOTE INDICATING ROTO ROTAMETER)
RADIO-ACTIVE & AQUEOUS WASTE STORAGE
PLUTONIUM SOLUTION
URANIUM SOLUTION
SOLVENT WASH AQUEOUS WASTE
COLUMN PULSER OR DRIVE PISTON FOR REMOTE HEAD PUMP
FLOW CONTROL MOTOR VALVE MAY BE REMOTELY OPERATED
TO PLUTONIUM PROCESSING
TO URANIUM PROCESSING
TO WASTE DISPOSAL

Figure 23-5-2. Typical processsing flow sheet for separation of plutonium, uranium, and fission products by solvent extraction.

ADSORPTION OF RADIOCOLLOIDS

Carrier-free separation of radioisotopes by adsorption of radiocolloids is a concentration technique based upon the fact that radiocollodial aggregates often are formed in extremely dilute solutions when chemical conditions are such that precipitation normally would occur at higher concentrations. Such radiocolloids can be adsorbed on glass surfaces, silica gel, activated carbon, alumina, or paper, and then eluted with acids or complexing agents.

Fission product ^{95}Zr – ^{95}Nb forms a radiocolloid in strong nitric acid solutions. Advantage is taken of this to cause separations when the solution is passed through a column filled with silica gel or other adsorbent, where the radiocolloid is taken up. After thorough washing, the ^{95}Zr – ^{95}Nb is dissolved and removed by 5 percent oxalic acid passed through the column.

CONCENTRATION OF GASES

Two inert radioactive gases – xenon and krypton (xenon-131 and -133 and krypton-85) – are formed in the fission or uranium. Concentration of (recapturing of) these radioisotopes normally is accomplished in the following manner:

- Short irradiated ^{235}U is dissolved in solution. The xenon and krypton made are forced through activated charcoal traps colled with liquid nitrogen and then placed into vials for shipment to customers.
- A problem in the treatment of uranium is the evolution of radioactive iodine gas. Although

iodine is not ordinarily a gas, under certain circumstances, it behaves as such and must be treated to ensure adequate control of releases to the environment. If long cooled or long decayed fuel is processed, the short-lived radioisotopes iodine decay to substantially lower levels.

- However, there are still longer-lived radioisotopes of iodine; for example, iodine-129, which has a long half-life and requires concentration.

EXTRACTION CHROMATOGRAPHY

Extraction chromatography is an analytical technique for the resolution of solutes, in which separation is made by differential migration in a porous medium and in which migration is caused by a flow of solvents. Essential requirements for the technique are –

- A column or strip of solid material that is insoluble in the solvents used. The solid material is termed the "support."
- A solution, in a suitable solvent, of the substances to be separated.
- A solvent, which is used to irrigate the column of material after the solution of the substances has been placed in the column. This solvent is known as the "eluting solvent," "eluant," or "mobile phase"; and the process of separating the absorbed solutes into zones is called "development."

One method of extraction chromatography employs a porous glass — bioglass — as the support. The glass is treated with a hydrophobic agent and saturated with HDEHP [Di (2-ethylhexyl) phosphoric acid]. Approximately 400 milligrams per gram of dry glass are used.

The bioglass is poured into a quarter-inch stainless steel column (approximately 18 inches in length) and allowed to settle. It is attached in a high-pressure ion-exchange system and loaded with two chemically similar elements (such as californium-252 and daughter curium-248). The dissolved elements then are loaded with nitric acid. The curium is eluted first with a 0.5 molar acid solution and elutes almost quantitatively in this solution. After the californium is removed with 2-molar nitric acid in 2 or 3 fractions, the bioglass is ready for regeneration and reuse.

The HNO_3 acidity can be made to a concentration of less than 0.2 molar if loaded on a small concentration column, and if each individual chemical to be concentrated (the californium and curium) is loaded on a separate column and stripped off with 4-or-6 molar nitric.

PROCESSING EQUIPMENT

The greatest difference between radiochemical and ordinary chemical operations rests almost entirely upon the fact that, in the former, penetrating radiations that can be injurious to operators and other nearby personnel are given off. Adequate shielding and a safe working environment must be provided for the control of radiation doses to workers and to the general public.

Most shielding is designed to absorb electromagnetic gamma or x-radiation. Gamma radiation is absorbed in matter by a number of processes known as the "photoelectric effect," "Compton recoil," and "pair formation," depending upon the energy of the radiation. Since the attenuation (stoppage) of gamma radiation is dependent upon collision with atoms, the denser the material, the greater the stopping power per unit thickness. Heavy materials such as lead are very good for shielding, although concrete is more popular because it is cheaper. There are some variations associated with atomic number; thus, perfectly regular sets of curves are not obtained when stopping power is plotted against photon energy for various elements.

Two general types of shielding are utilized – space shielding and localized shielding. Large operations, or those in which a great variety of equipment is built up and then removed in experimental work, are handled best by space shielding, of which the completely enclosed cell is the best example. Localized or unitized shielding is very useful for small operations, especially those in which permanent equipment is built and for which low down-time for maintenance work is required. Open-topped barricades may be used for up to about 10 curies of gamma emitters. With more intense sources, the scattering from the surrounding shielding and the air causes elevated radiation levels. The scattering effect is greater for the lower-energy gamma rays and X-rays than for the high-energy photons.

It is possible to have long, narrow holes or slots through heavy shields to accommodate tubing and control rods, provided that they are not directly in line with a radiation source.

Remote controls for operating valves or other mechanisms are operated by rod systems that contain universal joints or gears, or flexible cables passed through or over the shielding. Other mechanisms are hydraulically or pneumatically controlled. Selsyn and Servo motor electric controls also are employed.

Handling of radioactive fluids presents several problems concerned chiefly with storage, processing, and pumping equipment, again because of the radiation involved. Two methods for transfer of radioactive fluids are (1) pressure-vacuum on a closed system of tanks and (2) steam, air, or water jets for large equipment. Gravity flow is desirable in any plant, and nonradioactive chemical solutions and water almost always are added in this way from outside the shielding. Windows in shielding material contain a mineral oil that slows down the neutrons. The main shielding for gamma rays and the absorption of the neutrons is accomplished by lead glass, which has a high specific gravity.

Containment of radiation also is accomplished by creation of negative pressure zones inside the hot cells. If radioactivity leaks from the cell bank to the outside of the cell bank, it is completely surrounded by negative pressure; and the radioactivity will be contained in this space. The outer areas are under slightly less negative pressures, which, theoretically, provide a second containment area should the first one leak.

INSTRUMENTATION

A variety of instruments are utilized in the monitoring of the concentration processes. The important characteristics of the materials undergoing concentration include liquid level in a specific container, gravity, pressure (indicator instruments), and recording instruments to maintain a written record of the events involved in the various processes.

A wide variety of equipment is available for the purpose of measuring radiation and radioactivity levels. The choice of an instrument is a function of processes and radionuclides involved. The technician could expect to use portable ionization chambers, Geiger-Müeller count rate meters, electrometers of various types, automatic counting absorption curve machines, high-pressure gamma chambers, and many other similar instruments.

Difficulties in a process are signaled by tele-alarm systems that trigger bells and/or buzzers when liquid levels drop below proper level or when pressure increases. With instrumentation at the main panel board in the operating room, operating personnel can measure temperatures in various tanks, in different processes. Radiation alarms monitor the larger process installations.

As a safety feature, critical instruments can be duplicated in several areas in order that if a building becomes contaminated, either through malfunction of instruments or possible leakage from radioactive materials from the cell bank, operations personnel and the laboratory shift supervisor are informed and can take proper precautions immediately.

Panel boards often are set up in the form of a flowsheet diagram. Instruments are represented in the diagram in order that the appropriate personnel can determine exactly where they are located in each particular diagram. This system allows an observer to locate areas in which high radiation levels are occurring.

Alpha detectors are utilized in laboratory scale radioactivity monitoring when transplutonium elements such as curium, americium, berkelium, californium, fermium, and einsteinium are handled. These instruments are equipped with a thin mylar window across a silicon diode. As a drop of elutant from an ion-exchange column, for example, drops in front of the window, the alpha activity in that drop is monitored in the diode. The impulse then goes to a pre-amplifier and to a count rate meter. Becuase of the mylar window, flow through an alpha detector of this type is very sensitive to pressure. This sensitivity restricts its use to systems in which there is no pressure drop across the window severe enough to rupture it and to allow radioactivity to reach the detector.

An alpha detector can be converted to a neutron detector if a polyethylene cap is placed over the end of the detector. Beta-particle detection may be accomplished by use of a small ion chamber penetrated by relatively thin-walled vinyl plastic tubing. The beta particles that get through the vinyl tubing can be detected by the ion chamber. Gamma activity generally is monitored by ion chambers in the cells or in gloveboxes.

PROCESS PROCEDURES AND METHODS

"Process procedures and methods" refer primarily to the adherence to a complete written procedure and data log. The strict compliance to standard procedures ensures not only qualitative integrity of the process, but quantities' validity in terms of instrument calibration and data access.

The written log is of primary importance in terms of safety. In this log, the technician records every detail of the process, whether it be a manipulation, opening of a valve, addition of a liquid, or preparation of a solution. The log allows personnel on different shifts to review the events within the cell and provides some continuity between different technicians. The logs often are step-by-step procedures, and the technician initials each step as it is completed.

Procedure sheets differ from facility to facility, depending on the nature of the operations and the type of materials being handled, so that no standard format exists. The technician should record any unusual event during the procedure and should notify the appropriate personnel immediately. Such information as time, amount, and temperature are recorded in the logs.

EXERCISES

1. Write a descriptive paragraph on each of the following concentration methods:
    - Precipitation.
    - Distillation.
    - Ion-exchange.
    - Solvent extraction.
    - Concentration of a gas.
    - Crystallization and adsorption of radiocolloids.
2. Explain the importance of rare earth metals in the nuclear field.

MATERIALS

100 ml, 4% Dialex 50 WX4 resin (100 mesh).
400 ml, 6-molar HCl.
pH paper.
500 ml distilled water.
Approximately 0.5 g neodymium oxide (for Procedure I).
Approximately 0.5 g praseodymium oxide (for Procedure I).
10 g each of diethylene, triamine, and pentacetic acid
    (dtpa) made up to a liter and dissolved with ammonium
    hydroxide to make a pH of 7.
25 ml weak oxalic acid.
A balance accurate to milligrams.
Stop clock.
Filter paper.
Glass wool.
Watch glass.
Bunsen burner.
Ceramic triangle.
Ringstand.
500-ml graduated cylinder.
500-ml beaker.
100-ml buret.
0.5 g of either neodymium or praseodymium (for Procedure II).
3,000 ml distilled water.
400 ml HCl.

PROCEDURES

In the following laboratory procedures, nonradioactive chemical are used as stand-ins for radioactive chemicals. Many of the radioactive chemicals are prohibitively expensive as well as being so radioactive as to require shielded cells, manipulators, gloveboxes, etc. The rare earths are typical substitutes for the actinides. The stable isotopes of a particular element also can be safely substituted to reduce risk in the laboratory.

PROCEDURE I: CATION EXCHANGE SEPARATION OF RARE EARTHS

This exercise will demonstrate to the student how two elements can be separated and concentrated by the process of cation exchange separation.

1. Mix 200 ml of 6 molar HCl with 100 ml of 4% Dialex 50 WX4; stir the solution, let it settle, decant; repeat. (This procedure removes any residual cations that are on the resin to begin with.)
2. Add 200 ml of distilled water; settle, decant. Repeat unitl pH of the water is neutral (7.0-7.5). The pH can be checked with pH paper.
3. Pack glass wool near the bottom of the 100-ml buret (to prevent resin from going out the buret).
4. Place 75 ml of the treated resin into a 100-ml buret. Let resin settle.
5. Weigh the neodymium oxide and praseodymium oxide accurately to the nearest milligram. Record the weight of the two oxides in Data Table 23-5-1.
6. Mix the two rare earths (neodymium oxide and praseodymium oxide) together.
7. Dissolve this mixture in just enough HCl to get them into solution and still have less than 2/10 molar acid remaining. (The rare earths will load better out of a very weak solution; otherwise, one would be loading

hydrogen as well as the rare earth ions).

8. Pour the rare earths and weak acid solution into the column; allow them to load.
9. Wash the column with 25 ml of distilled water.
10. Pour 10 ml of the dtpa into the ion-exchange column. The flow should be 10 ml/minute. (The student can regulate flow with a stop clock.)
11. Elute the solution at the rate in Step 10. The dark color loaded on top will begin to resolve itself into two colors. The greenish color is praseodymium and the lavender is neodymium.
12. Allow eluant from the column to drip into a weak solution of oxalic acid. When a precipitate begins forming in the oxalic acid, the neodymium is beginning to come off.
13. Filter the precipitate. Dry the precipitate by placing it on the watch glass and, supported by the ring stand, heating gently until all water has been evaporated. Weigh the precipitate.
14. Compare the final weight of precipitate to original weight of neodymium and praseodymium. The weights should be the same.

PROCEDURE II: CONCENTRATION OF A PARTICULAR SUBSTANCE INTO A SMALLER VOLUME

1. Weigh the rare earth to nearest milligram. Dissolve either neodymium or praseodymium in enough HCl to make a solution, as was done in Procedure I. Record weight in Data Table 23-5-2.
2. Dilute solution with distilled water to 2 or 3 liters.

3. Pour solution through the column. (Use the column constructed for the first procedure and the resin regenerated following that procedure.)
4. Wash column with 25 ml of distilled water.
5. Make up a liter of 6-molar HCl; pour it through the column. (Watch colored band of rare earth move down the column.) One will be taking the rare earth off the column; volume will have been reduced to approximately 200 ml from original volumne of 2 or 3 liters.
6. Precipitate the solution in oxalic acid.
7. Filter the precipitate; fire it and weigh it, as in Procedure I. Record the weight in Data Table 23-5-2.
8. Compare final weight (7) to original weight (1).

DATA TABLES

DATA TABLE 23-5-1

(1) Mass of neodymium oxide ______
Mass of praseodymium oxide ______

(2) Final mass of precipitate ______

Total ______

DATA TABLE 23-5-2

(1) Original mass of neodymium oxide ______
Mass of praseodymium oxide ______

Total ______

Final mass of precipitate ______

REFERENCE MATERIALS

Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle, ERDA-76-43. Oak Ridge, TN: Technical Information Center, 1976.

Crouse, K.A. and Nelson F. Anion Exchange Studies of the Fission Products: Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Volume 7, Page 113, Session 9B 1, P/837, United Nations, 1956.

Fardy, J.J. and Chilton, J.M. Isolation of Plutonium in Cloride, Media 2, Solvent Extraction with Di (2-ethylhexyl) Phosphoric Acid. New York: Pergamon Press.

Gschneider, Carl A., Jr., Rare Earths – The Fraternal 15, USAEC Division of Technical Information, 1964 (Library of Congress Number 65-60546).

Oak Ridge National Laboratory Radioisotopes Procedures Manual, R and L 3633. Oak Ridge, TN: ORNL, 1964.

Parks, G.D. Mellors Modern Inorganic Chemistry. Revised edition. New York: John Wiley and Sons, Inc.

U.S. Atomic Energy Commission. Understanding the Atom Series. Oak Ridge, TN: Technical Information Center:

- Nuclear Terms: A Brief Glossary.
- Plutonium.
- Radioactive Waste.
- Synthetic Transuranium Elements.
- Chemistry of the Noble Gases.
- Your Body and Radiation.

TEST

1. Explain the purpose of, and necessity for, concentration techniques.

2. Describe at least four different concentration techniques discussed in this module.

3. Describe the equipment used for chemical concentrations.

4. Describe the instrumentation and monitoring of the concentration process.

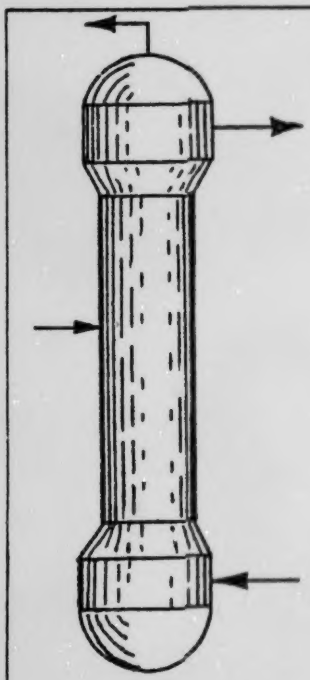
5. Explain the purpose of process procedures and process specifications.

6. Explain the reason for the use of nonradioactive chemicals as substitutes for radioactive materials in concentration models.

NUCLEAR TECHNOLOGY

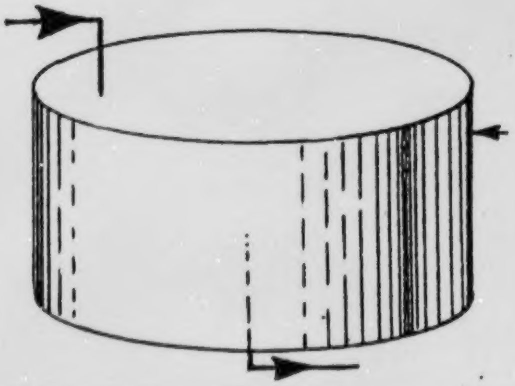
MODULE 23-6

DIFFUSION AND ENRICHMENT PROCESS



NUCLEAR CHEMICAL
PROCESSES

COURSE 23



CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
⇨ MODULE 23-6	Diffusion and Enrichment Process
MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

The conversion of uranium into uranium hexafluoride and the subsequent enrichment of the uranium hexafluoride gas to a predetermined percentage of the fissile ^{235}U isotope occurs both at the beginning and at the end of the nuclear fuel cycle. After uranium is mined, milled, and converted to "yellowcake" – a crude uranium concentrate containing between 70% and 90% U_3O_8 – it is converted to uranium hexafluoride gas. This gas then is sent to separation plants for isotope enrichment. At present, the UF_6 gas is enriched by the gaseous diffusion process, although other processes, such as plasma and laser-separation processes, are being investigated. After ^{235}U enrichment, the gas is converted into uranium dioxide. This substance is compacted into pellets, the pellets arranged in stacks in fuel assemblies, and the assemblies shipped to nuclear plants for use as reactor fuel.

After use, the spent fuel may be shipped to a reprocessing plant. Other modules in this course have described the process of shearing the fuel assemblies, recovering material by solvent extraction, and ion exchange. The uranyl nitrate solution that is recovered from the spent fuel by these various processes is converted to uranium hexafluoride. This substance may be sent to an enrichment plant, where the cycle begins anew.

This module describes the processes of uranyl nitrate conversion and uranium enrichment. Although the gaseous diffusion process is emphasized, other historical and future processes are discussed.

MODULE PREREQUISITES

The student should have completed courses in chemistry, algebra, and Course 1, "Radiation Physics"; Course 2, "Radiation Protection I"; Course 11, "Radiation Detection and Measurement"; and Course 17, "Radiation Protection II."

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Construct flowsheets that depict two processes for the conversion of uranyl nitrate to uranium hexafluoride.
2. Describe the equipment and processes used with these two flow sheets.
3. Describe equipment and processes for the collection of uranium hexafluoride, for its further purification and for its preparation for shipment.
4. Draw a schematic of a gaseous diffusion stage, and explain from the schematic the process of gaseous diffusion.
5. Utilize equations that describe the separation factor of isotopes and the ideal point separation factor of the ^{235}U on opposite sides of a barrier to describe the separation of ^{235}U and ^{238}U, and to justify the necessity of many stages in a diffusion cascade.
6. List four reasons why the actual stage separation factor differs from the ideal point separation factor.
7. Define the term "diffusion cascade," and draw simple schematics of typical arrangements in gaseous diffusion plants.

8. Describe the gas centrifuge process.
9. List and describe two electromagnetic separation methods.
10. List four objectives of laser isotope separation.

SUBJECT MATTER

Whether recovered from spent fuel by the solvent extraction process or formed by dissolution of yellowcake in acid, uranium must have its ^{235}U content increased before it can be utilized for the fabrication of spent fuel elements. This uranium in the form of a uranyl nitrate solution, first must be converted to uranium hexafluoride (UF_6) before shipment to a gaseous diffusion plant for enrichment. Figure 23-6-1 contains two typical flowsheets for the conversion of uranyl nitrate (UNH) to uranium hexafluoride (UF_6).

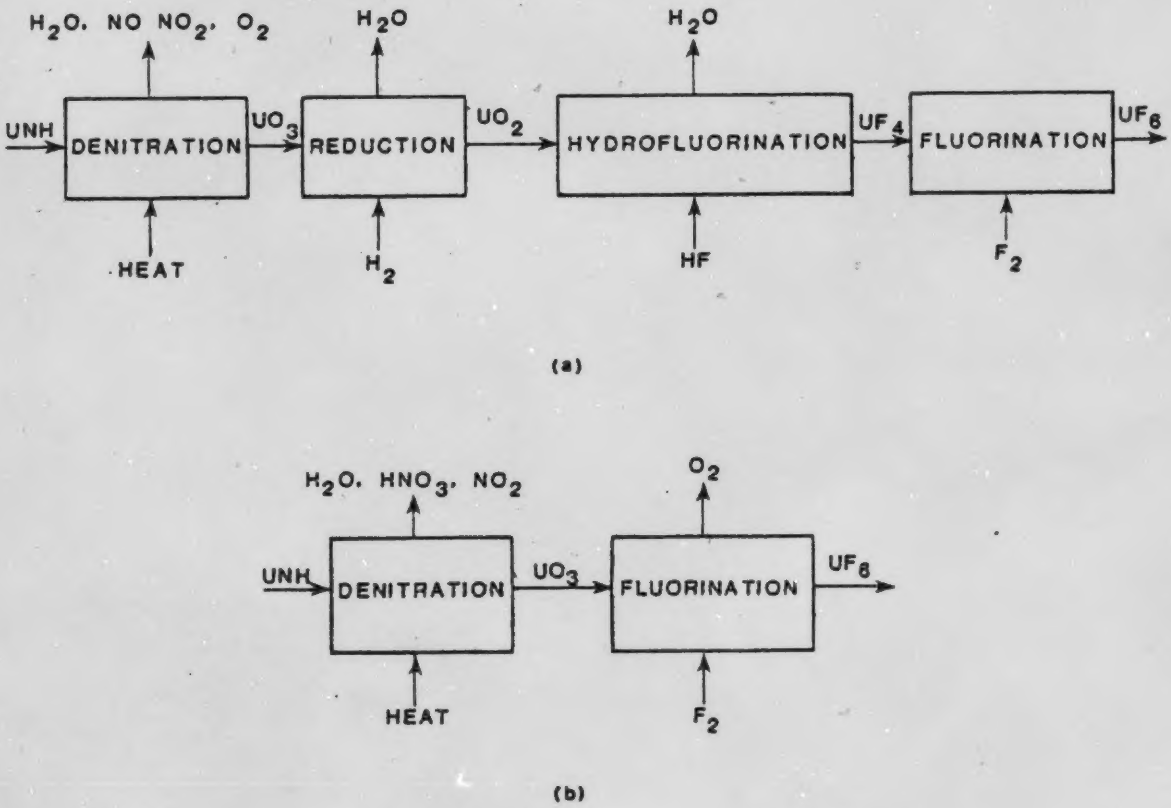

H2O. NO NO2. O2
H2O
H2O
UNH
DENITRATION
UO3
REDUCTION
UO2
HYDROFLUORINATION
UF4
FLUORINATION
UF6
HEAT
H2
HF
F2
(a)
H2O. HNO3. NO2
O2
UNH
DENITRATION
UO3
FLUORINATION
UF6
HEAT
F2
(b)

Figure 23-6-1. Two simplified flowsheets (a and b) for the conversion of UNH to UF_6.

Four steps are involved in the first process; two in the second. The first flowsheet (a) depicts a process similar to that for the large-scale production of uranium hexafluoride feed material for gaseous diffusion plants. The process illustrated in the second flowsheet (b) is simpler but has proved to be less economical than the four-step process.

DENITRATION

The first step in both processes is denitration, the conversion of a liquid uranyl nitrate solution to solid uranium trioxide. Denitration is accomplished by the heating of the uranyl nitrate solution to evaporate water and then by the decomposing of the remaining concentrated uranyl nitrate by the reaction described in Equation 23-6-1.

$$UO_2(NO_3)_2 \cdot H_2O \xrightarrow{\text{heat}} UO_3 + NO + NO_2 + O_2 + H_2O$$

Equation 23-6-1
(Equation = Eq.)

Denitration is carried out within any of several types of calciners. Calciners are mechanical devices utilized for heating materials to elevated temperatures in order to change the chemical or physical properties of the material by driving off vapors and gases to leave a powdery solid. The fluidized-bed calciner (Figure 23-6-2) is a popular design.

The term "fluidized bed" describes a bed of small solid particles kept in constant motion by a flow of gas or liquid

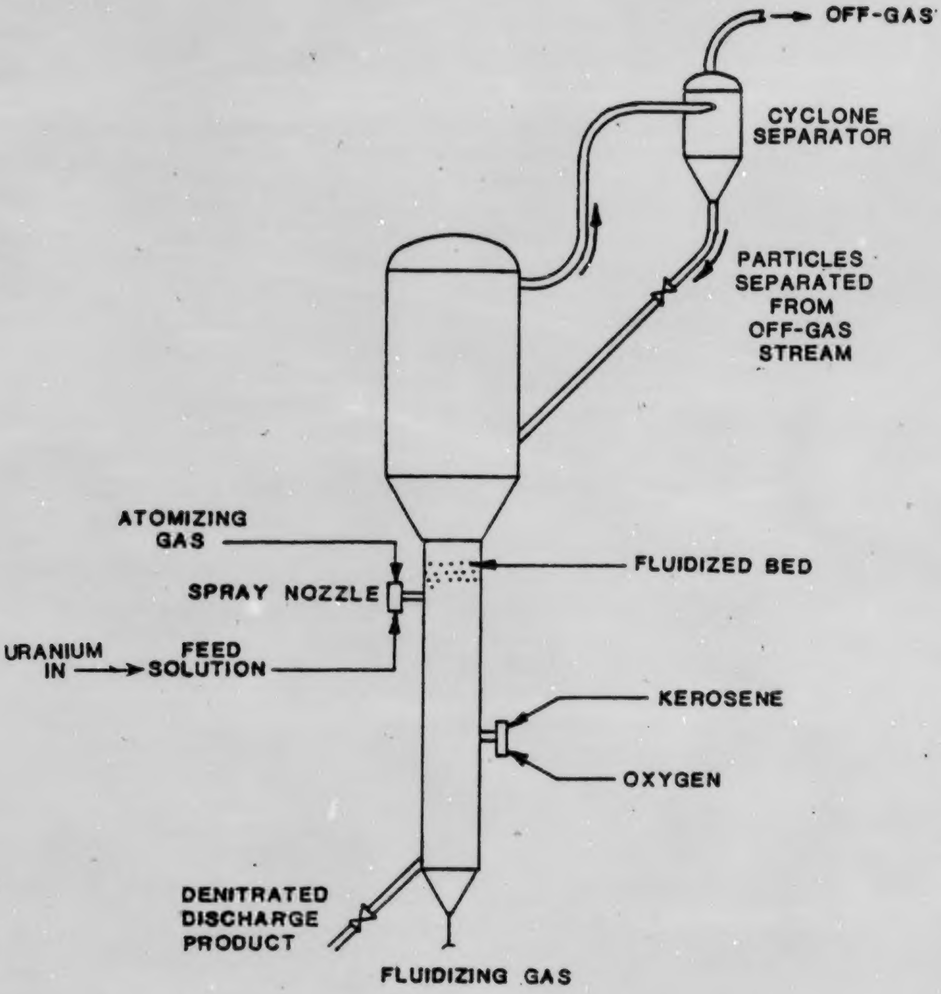

OFF-GAS
CYCLONE SEPARATOR
PARTICLES SEPARATED FROM OFF-GAS STREAM
ATOMIZING GAS
FLUIDIZED BED
SPRAY NOZZLE
URANIUM IN
FEED SOLUTION
KEROSENE
OXYGEN
DENITRATED DISCHARGE PRODUCT
FLUIDIZING GAS

Figure 23-6-2. Diagram of a fluidized-bed calciner.

upward through the bed. In this fluidized condition, the solid particles behave somewhat as a liquid or fluid. This fluidized bed offers good heat-transfer characteristics and relatively uniform temperature distribution, allowing reactions to be maintained at a fairly constant rate throughout the bed.

A common method for introduction of the feed solution into the calciner is through the use of a spray nozzle. The feed solution enters one side of the nozzle and flows through an opening in the center of the nozzle. Compressed gas enters the opposite side of the nozzle and discharges through an annular opening around the feed solution opening, thus atomizing the feed stream. The feed nozzle is located in the side wall of the calciner, sufficiently low on the vessel to provide for the nozzle being covered by the bed material at all times. When the nozzle is placed in such a position, deposition of solids on the walls of the calciner vessel is prevented.

The bed material is located in the lower section of the calciner. Beads of aluminum oxide or zirconium oxide commonly are utilized as seed materials for calciner beds involved in this type of process. The solids produced by evaporation and denitration of the uranyl nitrate coat the surfaces of the fluidized-bed beads and cause them to increase in size, forming beads of uranium trioxide. The fluidizing gas that keeps the bed material in motion is introduced at the bottom of the vessel. The bed is heated by the circulation of molten metal (such as NaK) through tubes located within the calciner bed. Typical operating temperatures of a denitration calciner bed are in excess of 300°C.

A cyclone separator located above the calciner is utilized for removal of entrained particles in the off-gas stream. Particles thus separated and trapped by the cyclone then are fed back into the calciner.

Operating conditions within the calciner must be regulated closely to yield the desired particle size, as well as the desired chemical and physical properties of the uranium trioxide produced by the denitration process. Important variables affecting the denitration process include, temperature, fluidization rate, feed concentration and feed rate, feed composition, and the operating characteristics of the feed nozzle.

REDUCTION OF URANIUM TRIOXIDE TO URANIUM DIOXIDE

Before the uranium trioxide produced in the nitration step can be converted to uranium tetrafluoride by hydrofluorination, it first must be reduced to uranium dioxide. This is only necessary when the first conversion process (section "a" of Figure 23-6-1) is used. In the second process (section "b" of Figure 23-6-1), uranium hexafluoride is produced by the reaction of uranium trioxide with fluorine gas. The reduction and hydrofluorination steps are bypassed.

Uranium trioxide is reduced by hydrogen to produce uranium dixoide as indicated in Equation 23-6-2. This exothermic

$$UO_3 + H_2 \longrightarrow UO_2 + H_2O \qquad \text{Eq. 23-6-2}$$

reaction is carried out at approximately 600°C.

Fluidized-bed reactors have been widely used for reduction of uranium trioxide. The bed material is composed mainly of uranium dioxide particles. Uranium trioxide particles are fed into the top of the bed. Inert gases plus hydrogen and nitrogen fluidize the bed. The uranium dioxide product is removed from the bottom of the bed. A typical fluidized-bed reduction unit is illustrated in Figure 23-6-3.

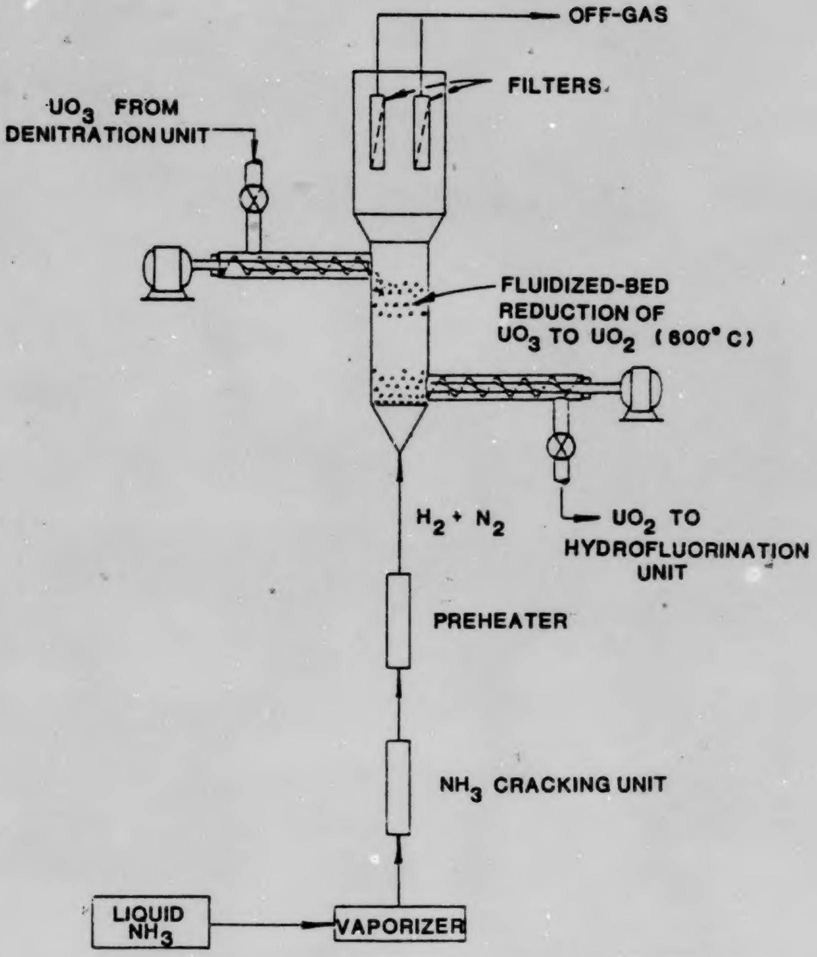

OFF-GAS
FILTERS
UO_3 FROM DENITRATION UNIT
FLUIDIZED-BED REDUCTION OF UO_3 TO UO_2 (600° C)
$H_2 + N_2$
UO_2 TO HYDROFLUORINATION UNIT
PREHEATER
NH_3 CRACKING UNIT
LIQUID NH_3
VAPORIZER

Figure 23-6-3. Schematic of a typical fluidized-bed reduction unit.

HYDROFLUORINATION OF URANIUM DIOXIDE

Uranium dioxide, produced in the reduction step, is converted to uranium tetrafluoride by the reaction of gaseous hydrogen fluoride as indicated by Equation 23-6-3.

$$UO_2 + 4HF \rightleftharpoons UF_4 + 2H_2O \qquad \text{Eq. 23-6-3}$$

Both stirred-bed and fluidized-bed reactors commonly are utilized for the hydrofluorination step.

The stirred-bed reactor consists of electrically-heated horizontal tubes about 16" in diameter and 22' in length. Stirrers located inside each tube mix and convey the UO_2 powder. Three units usually are operated in series. Uranium dioxide powder is fed to the top reactor, while anhydrous hydrogen fluoride gas is fed to the bottom unit and flows countercurrently to the flow of the powder.

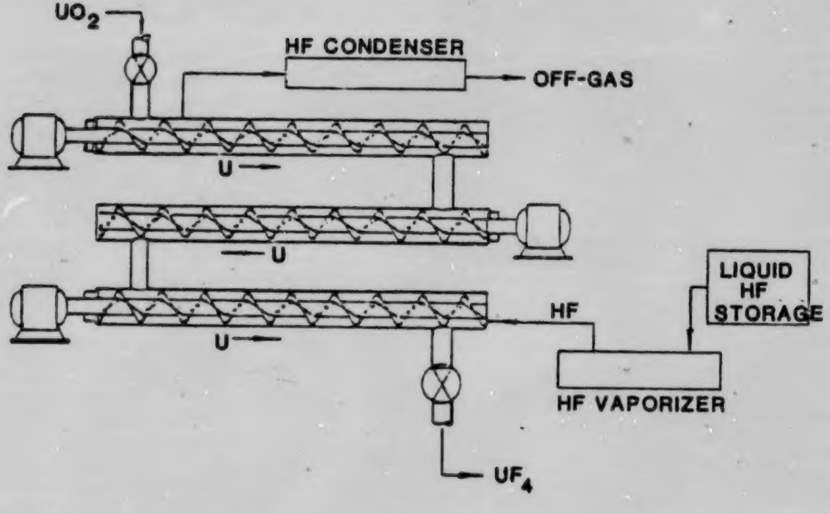
Two fluidized-bed reactors usually are arranged in series to increase the hydrogen fluoride efficiency. Uranium dixoide is fed to the first hydrofluorinator near the top of the bed, and a mixture of uranium tetrafluoride and unreacted uranium dioxide is withdrawn near the bottom of the first hydrofluorinator. This mixture then is fed to the upper section of the second hydrofluorinator. Uranium tetrafluoride is withdrawn at the bottom of the second hydrofluorinator.

The gaseous HF used in the hydrofluorination reaction also serves as the fluidizing gas for the fluidized-bed units. The hydrogen fluoride gas enters the second reactor first and thus flows countercurrently to the flow of the UO_2 powder.

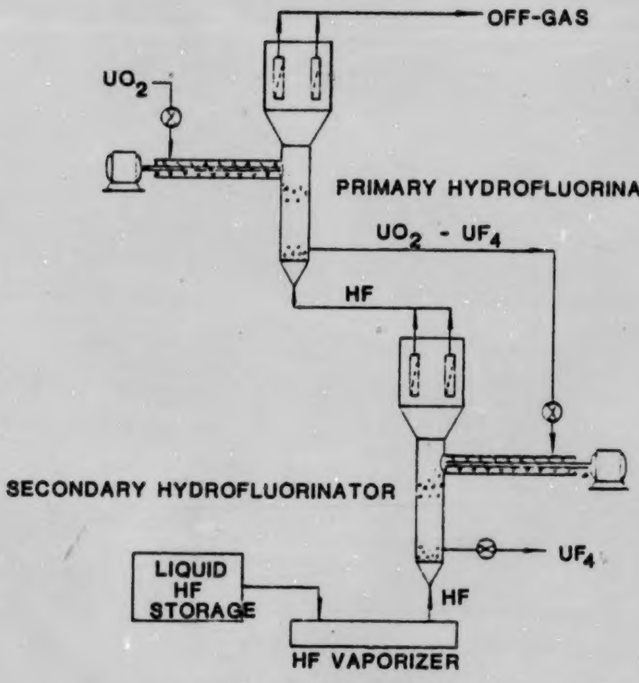
Both the stirred-bed and the fluidized-bed hydrofluorination systems are operated at approximately 475°C. Operating temperature and the amount of excess HF gas present are important variables that affect product quality.

The gaseous hydrogen fluoride used in the process is produced by vaporization of liquid hydrogen fluoride (vapor point 19.4°C). Since hydrogen fluoride is extremely corrosive and toxic, special treatment is necessary for the removal of the gas from the off-gas stream. HF is particularly corrosive in regard to fiberglass filters, which typically are used in off-gas treatment. Typical methods for removal of the HF gas from the off-gas stream consist of scrubbing with potassium hydroxide (KOH) solution and by reaction in beds of soda-lime or sodium fluoride (NaF).

Schematic diagrams that represent the two types of hydrofluorination reactors are given in Figure 23-6-4.


UO_2
HF CONDENSER
OFF-GAS
U
U
U
HF
LIQUID HF STORAGE
HF VAPORIZER
UF_4

Stirred-bed Hydrofluorination System


OFF-GAS
UO_2
PRIMARY HYDROFLUORINATOR
UO_2 - UF_4
HF
SECONDARY HYDROFLUORINATOR
UF_4
LIQUID HF STORAGE
HF
HF VAPORIZER

Fluidized-bed Hydrofluorination System

Figure 23-6-4. Schematic diagrams of a stirred-bed hydrofluorination system and a fluidized-bed hydrofluorination system.

FLUORINATION OF URANIUM TETRAFLUORIDE AND URANIUM DIOXIDE

As indicated by Figure 23-6-1, uranium hexafluoride (UF_6) is produced by the reaction of fluorine gas (F_2) either with uranium tetrafluoride (UF_4) or with uranium trioxide (UO_3). These two reactions are displayed in Equations 23-6-4 and 23-6-5.

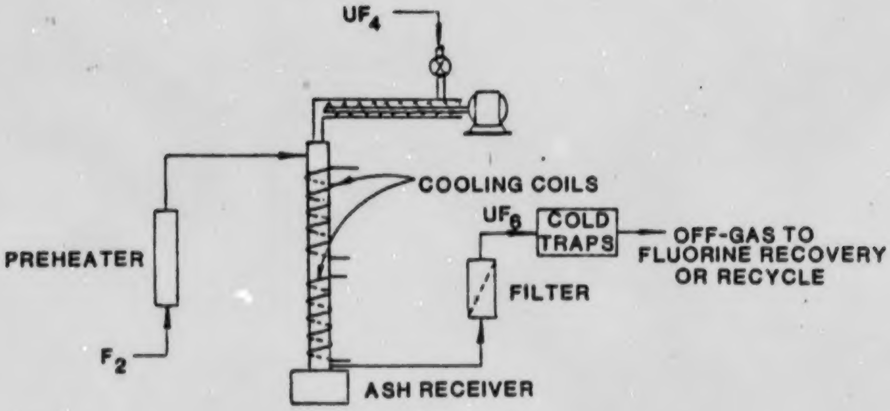
$$UF_4 + F_2 \longrightarrow UF_6 \qquad \text{Eq. 23-6-4}$$

$$2UO_3 + 6F_2 \longrightarrow 2UF_6 + 3O_2 \qquad \text{Eq. 23-6-5}$$

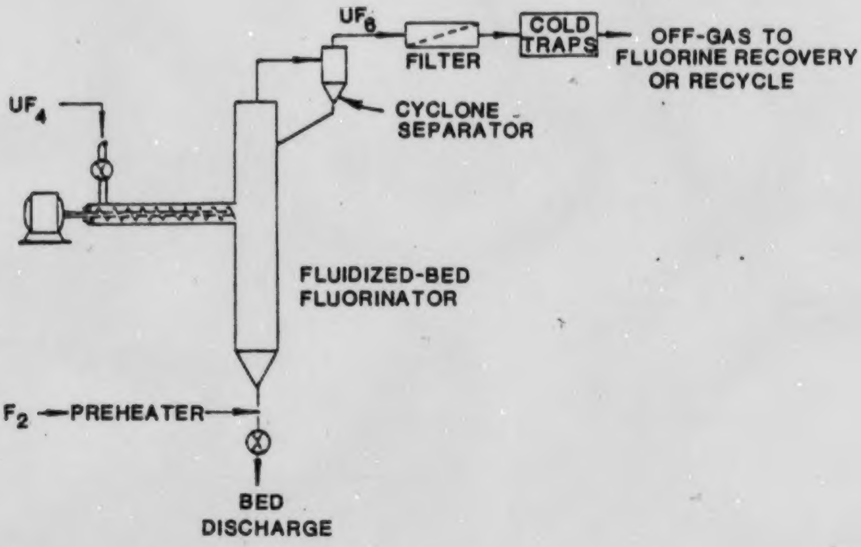
Both reactions are highly exothermic, and cooling is required to maintain the desired reaction temperature. The UF_6, in both cases, is produced in the form of a gas. Special equipment is necessary for the collection of the product gas, for the generation of the fluorine, and usually for further purification of the UF_6 product.

Uranium trioxide usually is fluorinated in a fluidized-bed reactor, and uranium hexafluoride is fluorinated by use of either the fluidized-bed reactor or the tower reactor. Both types of fluorination reactors are illustrated in Figure 23-6-5.

A typical tower reactor is constructed of a vertically-mounted, 8"-diameter Monel pipe. Cooling coils are wrapped around the pipe exterior for the removal of excess reaction heat. A fine powder of UF_4 is introduced at the top of the tower, along with F_2 gas that has been heated to approximately 300°C. The fluorine gas quickly reacts with the uranium


UF$_4$
COOLING COILS
UF$_6$
COLD TRAPS
OFF-GAS TO FLUORINE RECOVERY OR RECYCLE
PREHEATER
FILTER
F$_2$
ASH RECEIVER

Fluorine Tower Reactor


UF$_6$
FILTER
COLD TRAPS
OFF-GAS TO FLUORINE RECOVERY OR RECYCLE
UF$_4$
CYCLONE SEPARATOR
FLUIDIZED-BED FLUORINATOR
F$_2$
PREHEATER
BED DISCHARGE

Fluidized-Bed Fluorinator

Figure 23-6-5. Schematic diagram of a fluorination tower and a fluidized bed for production of UF_6 and UF_4.

tetrafluoride to produce uranium hexafluoride. The temperature of the reactor is regulated in a range of 454°C to 538°C. The primary reaction converts about 98% of the UF_4 to UF_6, and the remaining 2% must be recycled.

In the fluidized-bed reactor, UF_4 or UO_3 is fed into a fluidized-bed of inert material, such as fused alumina or calcium fluoride, at a temperature range of 427°C to 537°C. A mixture of fluorine and an inert gas (nitrogen, oxygen) is utilized for fluidization. The excess of fluorine gas in the fluidization gas mixture reacts with the feed stream to quickly convert the feed material to UF_6, preventing the accumulation of feed material on the bed.

Since uranium hexafluoride is a solid at room temperature, thermal regulation of all lines transporting the uranium hexafluoride is necessary to prevent the formation of solid plugs in the transfer lines.

COLLECTION OF URANIUM HEXAFLUORIDE

Gaseous uranium hexafluoride produced in the fluorination process normally is collected by a method known as "cold-trapping." Cold traps usually are operated in pairs attached in series. The primary cold trap is regulated at approximately -18°C and will remove the majority of the gaseous UF_6 by lowering the temperature of the gas, thus converting the UF_6 to solid form and collecting the solidified UF_6. The secondary trap in the series is operated at approximately -60°C and will collect most of what the first trap missed.

At least two sets of traps are required for continuous operation; one set is on line while the other set is being

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emptied. The traps to be emptied are disconnected from the line by closing the inlet and outlet valves of the trap and shutting off the refrigerant gas supply. Heaters built into the trap then can melt the solid UF_6 and facilitate its transfer to a product cyclinder.

Figure 23-6-6 depicts a typical cold trap. The cold trap is possessed of both heating and cooling coils on its outer surface and is enclosed by a thermal insulating layer of glass.

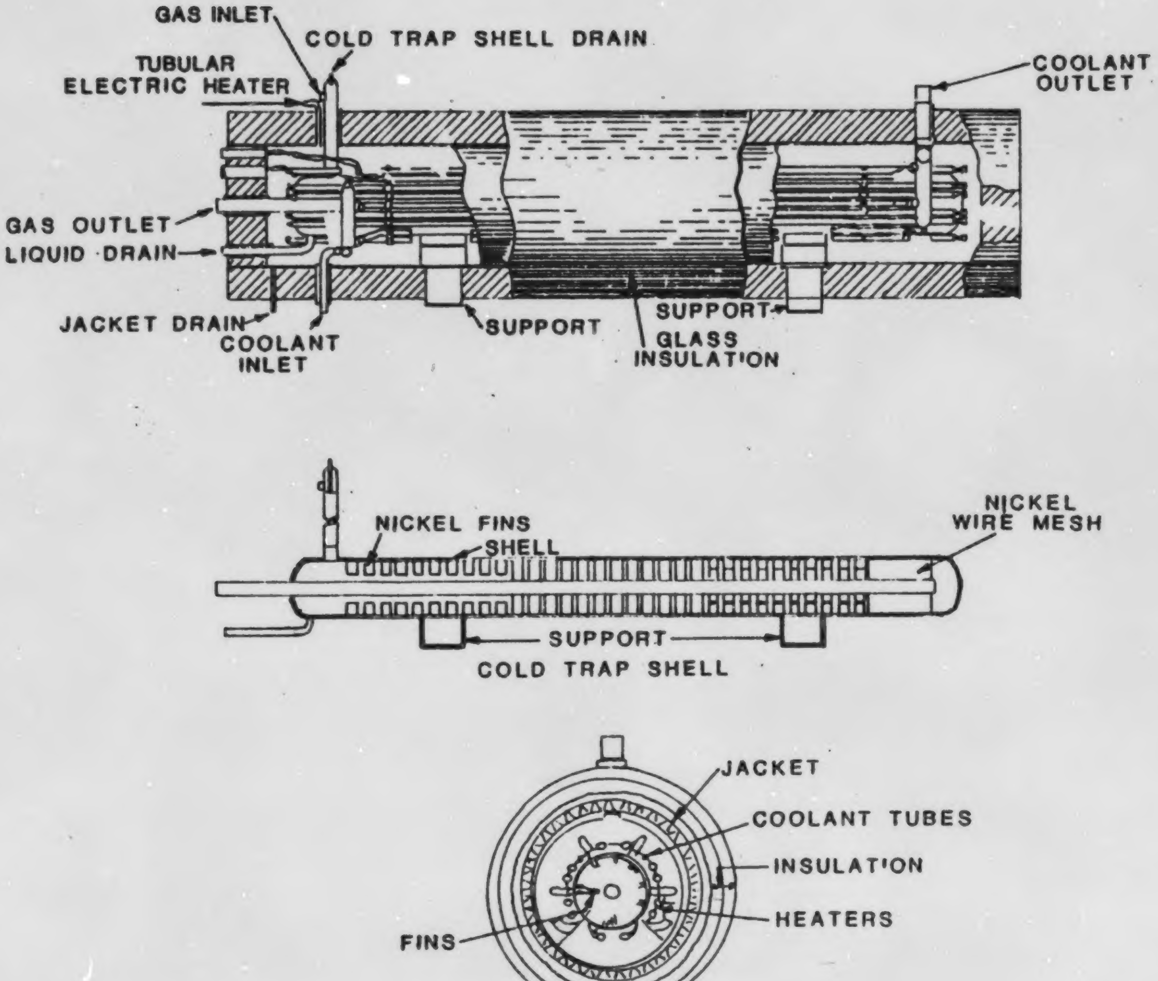

GAS INLET
COLD TRAP SHELL DRAIN
TUBULAR ELECTRIC HEATER
COOLANT OUTLET
GAS OUTLET
LIQUID DRAIN
JACKET DRAIN
COOLANT INLET
SUPPORT
SUPPORT
GLASS INSULATION
NICKEL FINS
SHELL
NICKEL WIRE MESH
SUPPORT
COLD TRAP SHELL
JACKET
COOLANT TUBES
INSULATION
HEATERS
FINS

Figure 23-6-6. Cold trap for the collection of UF_6.

PURIFICATION OF URANIUM HEXAFLUORIDE

Uranium not completely purified in the solvent extraction phase of reprocessing may be further purified after conversion to uranium hexafluoride. The major portion of impurities present in the hexafluoride consists of volatile fission products and any corrosion products volatilized in the fluorination process. The two methods commonly used for purification of uranium hexafluoride are distillation and the use of solid sorbents.

A typical UF_6 distillation system, as illustrated in Figure 23-6-7, consists of a vertical column that contains the liquid and vapor phases. A reboiler is located at the bottom of the column for boiling the liquid to produce the vapor phase, which travels up the column. A set of condensers located at the top of the column condense the vapor phase back into the liquid for collection. The first condenser that the vapor reaches is a reflux condenser, which allows a portion of the condensed vapor to drain back into the column, where the liquid contacts the vapor phase. In general, the reflux rate will have a proportional effect upon the quality of the separation of uranium hexafluoride from its impurities.

The UF_6 feed enters the distillation system at about the center of the column. Those impurities that have a boiling point below that of the UF_6 will concentrate in the upper portion of the column and can be removed at that point. Those impurities that are less volatile than the UF_6 will concentrate in the reboiler, from which it can be removed.

Important variables that influence the distillation process can be outlined as follows:

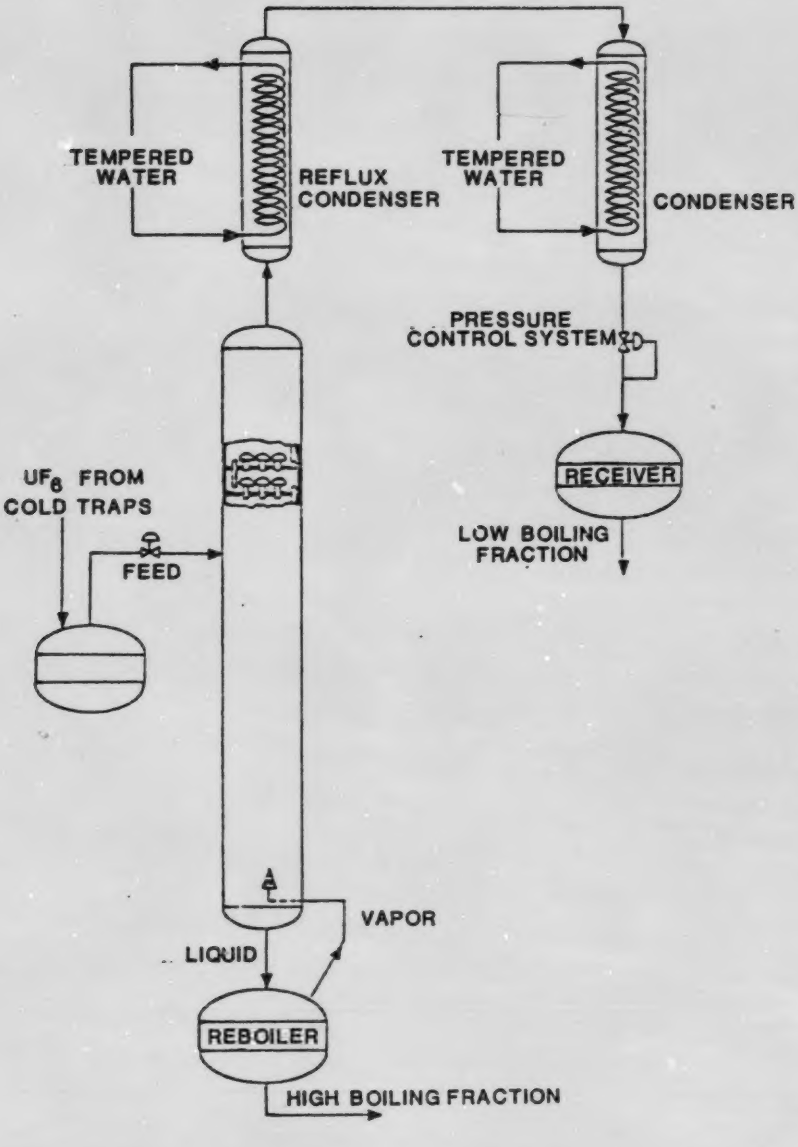

TEMPERED WATER
REFLUX CONDENSER
TEMPERED WATER
CONDENSER
PRESSURE CONTROL SYSTEM
RECEIVER
LOW BOILING FRACTION
UF$_6$ FROM COLD TRAPS
FEED
VAPOR
LIQUID
REBOILER
HIGH BOILING FRACTION

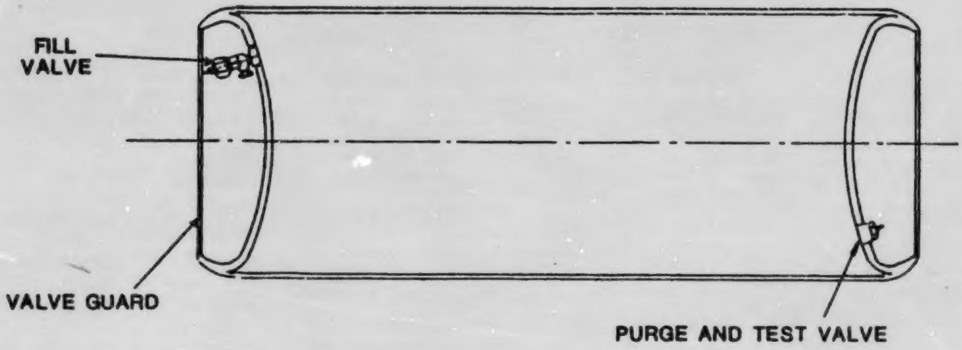
Figure 23-6-7. System for purification of UF$_6$ by distillation.

- Reboiler temperature, which determines the rate at which vapor is sent to the bottom of the column.
- Column temperature, which must be kept reasonably high to prevent freezing of the uranium hexafluoride.
- Condenser temperature, which must be low enough to condense the vapor without freezing it.
- Feed-rate to the column.
- Amount of liquid reflux and rate at which product and waste are removed from the column.
- Pressure at the condenser outlet.

Fission and corrosion products have been removed from UF_6 by contact with sodium fluoride (NaF) and magnesium fluoride (MgF_2). Two common impurities (technetium and neptunium) in uranium hexafluoride can be removed by passage of the UF_6 gas through a bed of MgF_2 at 100°C. Fluorides of plutonium, of corrosion products, and of such fission products as ruthenium and niobium can be removed by passage through beds of NaF at 400°C. Another method of purification is based upon the sorption of UF_6 on NaF at 100°C and desorption at 400°c.

SHIPMENT OF URANIUM HEXAFLUORIDE

After uranium hexafluoride has been purified, it must be placed into approved containers for shipment to a gaseous diffusion plant. Various standard cylinder designs have been approved. Figure 23-6-8 depicts a Model 30A cylinder that will hold approximately 2 1/2 tons of uranium hexafluoride.



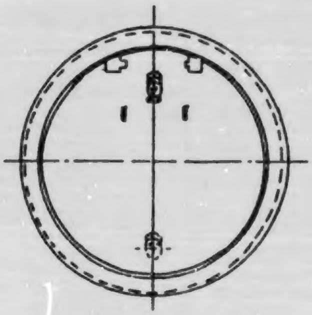


Figure 26-3-8. Model 30A cylinder.

Figure 26-3-9 depicts a typical cylinder-filling system. All the full lines are regulated to a range of 60°C to 68°C to prevent solidification of the UF_6. Steps in the cylinder-filling process can be outlined in the following sequence:

- The cylinder is inspected, evacuated, and weighed.
- Cylinder connections are completed, then purged and tested for leaks.
- The fill valves are opened to allow the liquid uranium hexafluoride to enter the cylinder.

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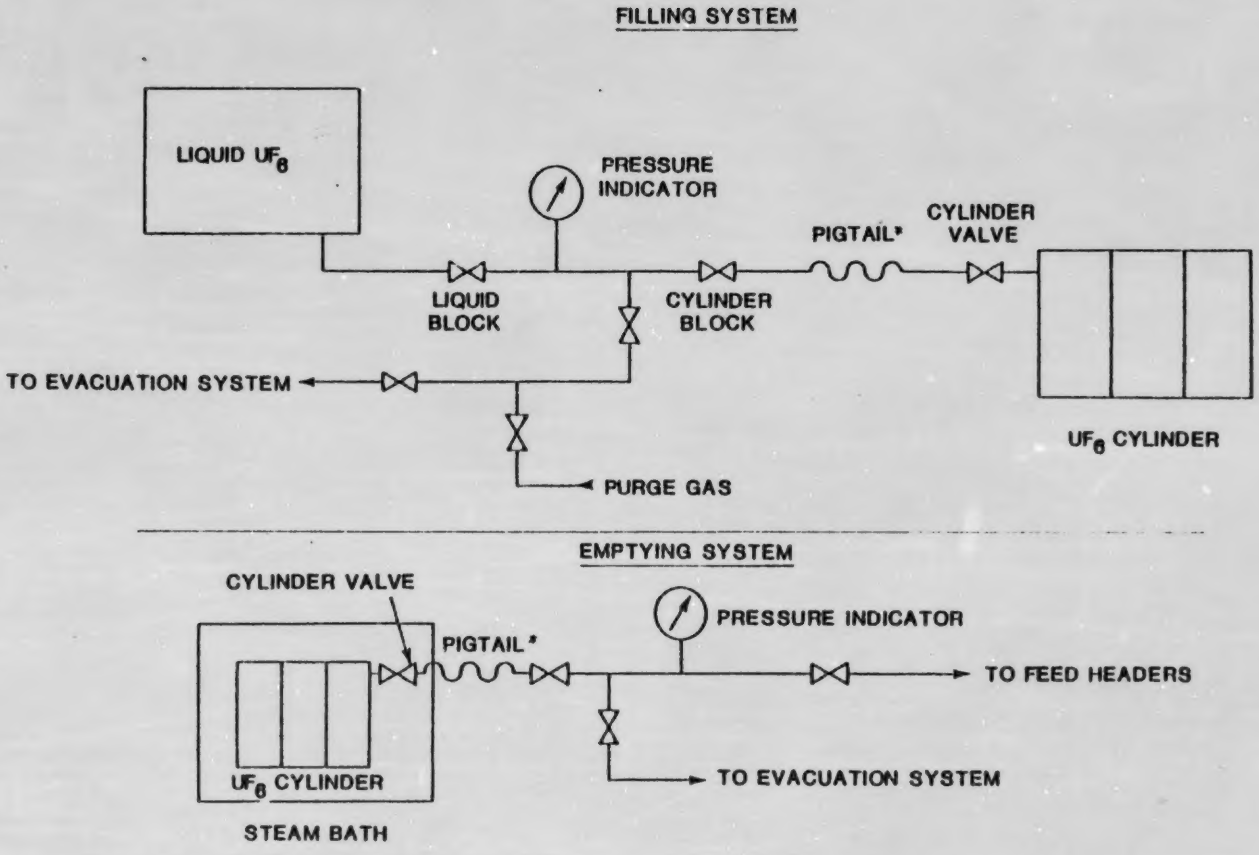
FILLING SYSTEM
LIQUID UF_6
PRESSURE INDICATOR
PIGTAIL*
CYLINDER VALVE
LIQUID BLOCK
CYLINDER BLOCK
TO EVACUATION SYSTEM
UF_6 CYLINDER
PURGE GAS
EMPTYING SYSTEM
CYLINDER VALVE
PIGTAIL*
PRESSURE INDICATOR
TO FEED HEADERS
TO EVACUATION SYSTEM
UF_6 CYLINDER
STEAM BATH

* SEMIFLEXIBLE TUBING CONNECTOR

Figure 23-6-9. A typical system for filling cylinders.

- After the cylinder has been loaded, the valves are closed, and all connections are purged.
- The cylinder then is disconnected and weighed.

Filled cylinders are not shipped until the uranium hexafluoride has solidified.

During the loading procedure, the cylinder being filled is maintained at 90°C to prevent solidification of the UF_6 and is weighed continuously to prevent overfilling. The cylinder is held on a dolly in a horizontal position to minimize the possibility of the cylinder being dropped. All filling operations are conducted behind barriers to protect the cylinder and associated piping from possible damage; and in the event of leakage, quick solidification of the UF_6 is accomplished by a mobile pressurized CO_2 system. All personnel working in close proximity to the cylinder are required to put on protective clothing and respiratory equipment.

THE GASEOUS DIFFUSION PROCESS

All naturally-occurring uranium contains a small fraction (0.72%) of the fissionable isotope ^{235}U; however, some types of nuclear plants, such as light water-moderated plants, require what is known as "enriched fuel" – fuel with a greater than normal content of ^{235}U. Because the nature of the isotopes of any given elemental species prevents the separation of those isotopes by chemical methods, a process called "gaseous diffusion" frequently is employed to increase the percentage of the ^{235}U isotope. This process is dependent upon the molecular motion of gases, with the lighter molecules possessing the higher velocities.

In the gaseous diffusion process, a mixture of $^{238}UF_6$ and $^{235}UF_6$ is introduced into a unit called a "gaseous diffusion stage." Such a unit is represented schematically in Figure 23-6-10.

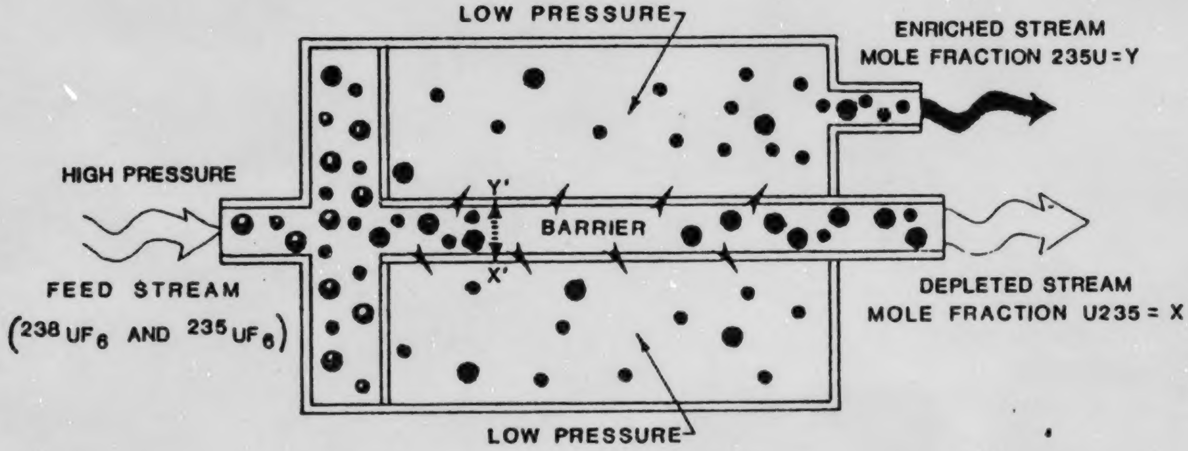
LOW PRESSURE
ENRICHED STREAM
MOLE FRACTION 235U = Y
HIGH PRESSURE
Y'
BARRIER
X'
FEED STREAM
($^{238}UF_6$ AND $^{235}UF_6$)
DEPLETED STREAM
MOLE FRACTION U235 = X
LOW PRESSURE

Figure 23-6-10. Gaseous diffusion stage.

The gas under high pressure is pumped through barrier tubes constructed of a thin, porous material that contains hundreds of millions of very small openings (pores) per square inch. The average diameter of these pores is about 50 µm (5×10^{-5}m). Due to the pressure differential between the barrier tube containing the pressurized feed stream and the low-pressure chamber surrounding the tube, the gas molecules gradually diffuse through the barrier and into the chamber. Since the $^{235}UF_6$ molecule is lighter than the $^{238}UF_6$ molecule, the $^{235}UF_6$ gas molecules diffuse across the barrier at a higher rate than the $^{238}UF_6$ molecules. The gas that flows through the barrier first, then, will be richer in the ^{235}U isotope, and that portion of the gas within the barrier tube will be richer in the ^{238}U isotope.

The degree of separation accomplished in one gaseous diffusion stage is very small, thus the process must be repeated many times before practical enrichment is attained. A gaseous diffusion plant, therefore, consist of hundreds of similar stages, connected in series, and called "diffusion cascades."

The degree of enrichment of the ^{235}U isotope is dependent upon the number of stages contained in the overall system. Depleted uranium, known as "tails," is withdrawn at the bottom of the cascade. Gaseous diffusion plants are located at Oak Ridge, Tennessee; Paducah, Kentucky; and Portsmouth, Ohio.

THE THEORY OF GASEOUS DIFFUSION

Substances that differ only in isotopic content differ very little in chemical and physical properties; however, these small differences do provide a sufficient basis for isotopic separations. These differences among isotopic components are described in terms of a separation factor (α) defined by the relation given by Equation 23-6-6.

$$\alpha = \frac{r}{r^1} \qquad \text{Eq. 23-6-6}$$

where:

α = separation factor.
r = isotope ratios before separation.
r^1 = isotope ratios after separation.

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In almost all cases, the value of α for single-stage diffusion operations differs from unity only in the second or third decimal place.

In the separation of uranium isotopes by gaseous diffusion of uranium hexafluoride, the actual separation factor that relates the concentration of the ^{235}U isotope on opposite sides of the barrier is expressed by Equation 23-6-7.

$$\alpha = \left(\frac{y^1}{y - y^1}\right)\left(\frac{x^1}{1 - x^1}\right) \qquad \text{Eq. 23-6-7}$$

$$= \frac{M(^{238}UF_6)}{M(^{235}UF_6)}$$

$$\alpha = 1.00429$$

where:

y^1 = the mole fraction of ^{235}U in the process gas adjacent to the barrier on the low-pressure side.

x^1 = the mole fraction of ^{235}U adjacent to the barrier on the high-pressure side.

The ideal point separation factor (α^1) is given approximately by the equation:

$$\alpha^1 \simeq \sqrt{\frac{\text{diffusion rate } ^{238}U}{\text{diffusion rate } ^{235}U}} \qquad \text{Eq. 23-6-8}$$

Since the rate of effusion of any isotopic species through a barrier is inversely proportional to the square of its molecular weight, Equation 23-6-8 may be expressed in the form of Equation 23-6-9.

$$\alpha^1 \simeq \sqrt{\frac{\text{molecular wt } ^{238}\text{U}}{\text{molecular wt } ^{235}\text{U}}} \qquad \text{Eq. 23-6-9}$$

$$\simeq \sqrt{238/235}$$

$$\alpha^1 \simeq 1.00636$$

This ideal point separation factor stipulates a perfect barrier and zero back pressure on the low-pressure side of the barrier. Considering the requirements, this ideal point separation factor is rarely, if ever, achieved.

The actual stage separation factor differs from the ideal point separation factor because of the nonhomogenous nature of the barrier, which contributes to variability in barrier efficiency, back pressure, mixing efficiency, and the varying concentrations of the streams leaving the stage, relative to the point concentrations within the stage.

Because the single-stage separation factor is so small, provisions must be made for many stages, arranged in a diffusion cascade, to attain the desired degree of enrichment.

THE DIFFUSION CASCADE

A "cascade" (Figure 23-6-11) is an assembly of separating stages (as illustrated in Figure 23-6-10) utilized to accomplish a specific separation. Several arrangements of stages within a cascade are possible. Some specific examples of arrangement are illustrated in Figures 23-6-12 through 23-6-14.

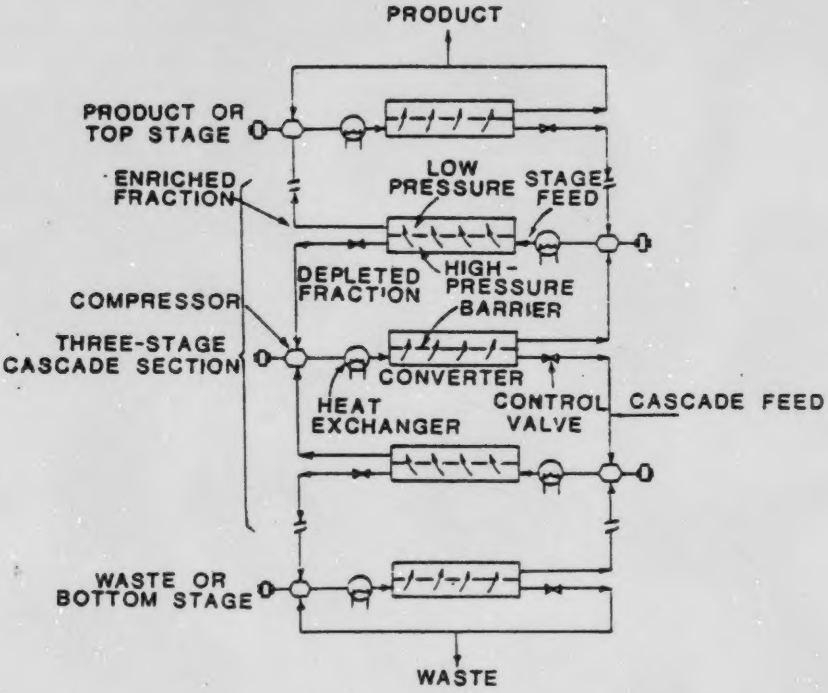
PRODUCT
PRODUCT OR TOP STAGE
ENRICHED FRACTION
LOW PRESSURE
STAGE FEED
DEPLETED FRACTION
HIGH-PRESSURE BARRIER
COMPRESSOR
THREE-STAGE CASCADE SECTION
CONVERTER
HEAT EXCHANGER
CONTROL VALVE
CASCADE FEED
WASTE OR BOTTOM STAGE
WASTE

Figure 23-6-11. A cascade of gaseous diffusion stages.

The simplest cascade (Figure 23-6-12) is composed of individual separation stages connected in series. The series-parallel cascade (Figure 23-6-13) is composed of many identical separating elements with throughputs that are small compared to the cascade interstage flow. A cascade composed of four-stream separating devices (Figure 23-6-14) can mix upflows and downflows of feed streams and redistribute them between each bank of columns.

Cascade arrangement within a gaseous diffusion plant is critical. Designers have defined the ideal cascade and are attempting to design a system as close to the model as possible. The ideal cascade is one in which there is no mixing of streams of differing concentrations at the inlet to a separation stage to form the feed to that stage. Fortunately, well-designed, real cascades can approximate closely the ideal cascade.

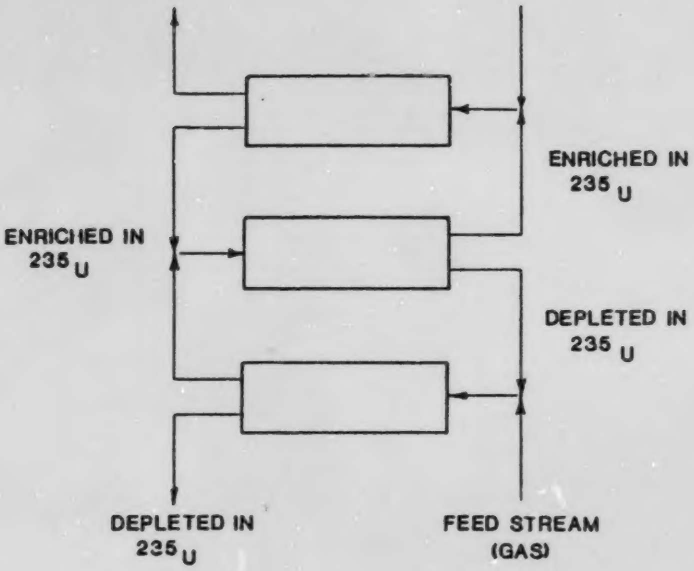
ENRICHED IN
^{235}U
ENRICHED IN
^{235}U
DEPLETED IN
^{235}U
DEPLETED IN
^{235}U
FEED STREAM
(GAS)

Figure 23-6-12. A cascade section composed of individual separation stages connected in series.

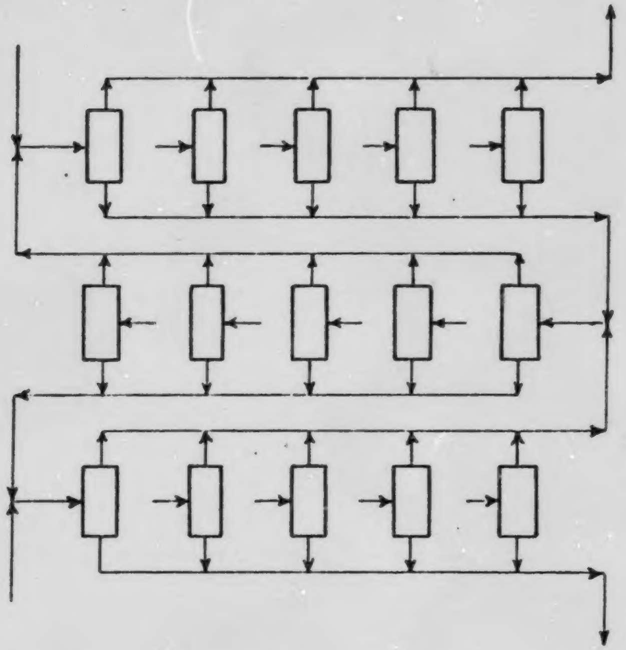

Figure 23-6-13. A cascade section composed of small separating elements (stages or columns) connected in a series-parallel arrangement.

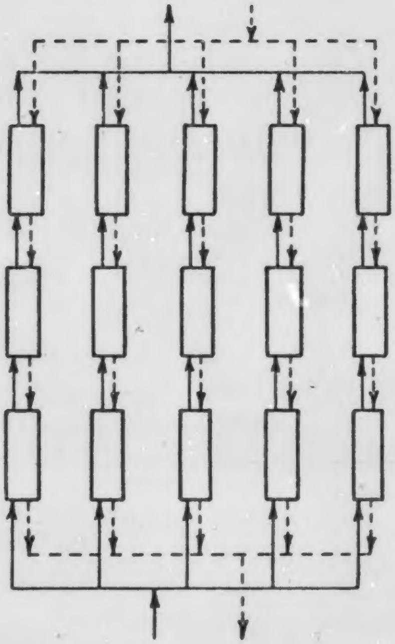

Figure 23-6-14. A cascade section composed of four-stream separating devices (countercurrent columns).

The actual operation of a diffusion cascade is illustrated simply in Figure 23-6-15.

The feed material, consiting of uranium hexafluoride with a natural abundance of 0.72% $^{235}UF_6$ in the case of natural uranium or some other abundance if the gas has been recovered from spent fuel, enters the cascade at an intermediate stage. The $^{235}UF_6$ enriched product is withdrawn from the enriching section, and the depleted waste is withdrawn from the bottom at the waste withdrawal point. Pumps circulate downflow gas from stage to stage to compress and circulate upflow gas.

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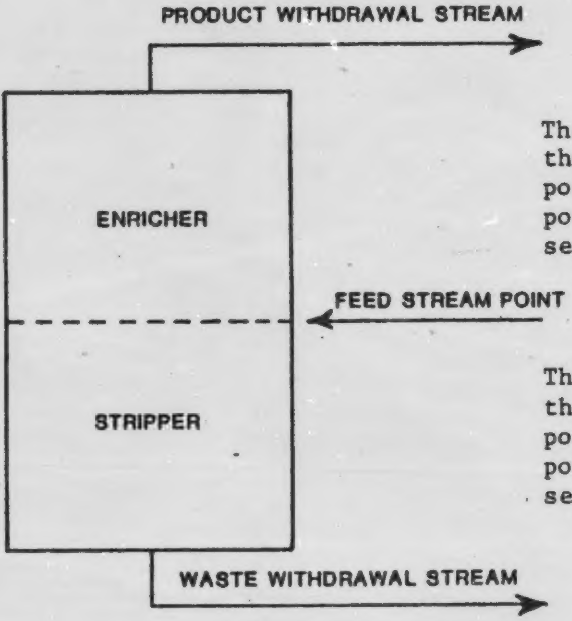


The section of the cascade above the feed point (between the feed point and the product withdrawal point) is called the "enriching section," or the "enricher."

The section of the cascade below the feed point (between the feed point and the waste withdrawal point) is called the "stripping section," or the "stripper."

Figure 23-6-15. A simple separation cascade.

OTHER ENRICHMENT PROCESSES

Alternatives to the gaseous diffusion process exist and include the gas centrifuge process, laser isotope separation, the plasma separation process, and the electromagnetic method. The gas centrifuge process is the most attractive alternative to gas diffusion.

THE GAS CENTRIFUGE PROCESS

Demonstration gas centrifuge facilities have been built and operated in many nations. The U.S. operates a gas centrifuge enrichment plant at Oak Ridge, Tennessee.

Figure 23-6-16 depicts an early-model gas centrifuge. The gas centrifuge is essentially a hollow, vertical cylinder spun on its long axis at high angular velocity. Gaseous uranium hexafluoride is fed to the centrifuge and accelerated to approximately the angular velocity of the rotor. Centrifugal forces cause steep pressure gradients to build up within the gas mixture, and ensuing pressure diffusion results in radial concentration of the different isotopes, with the light isotope being slightly enriched in the vicinity of the axis and the heavy isotope being slightly enriched in the vicinity of the rotor wall. Countercurrent gas centrifuges are of most interest; in them an axial convective circulation of the process gas is induced within the rotor in order to produce large end-to-end separation effects. The principal components of a countercurrent gas centrifuge are indicated in Figure 23-6-16. The centrifuge spins inside an evacuated casing. The introduction of the feed gas and the withdrawal of enriched and depleted streams are accomplished by means of stationary tubes at the axis of the rotor. Stationary scoops at the ends of the rotor extend into the rotating gas. The countercurrent circulation may be induced by the mechanical action of the unshielded scoop or by induced temperature differences between the ends of the rotor. The bowl is supported at the top by a magnetic bearing and at the bottom by a needle bearing, and is driven by an electric motor.

A gas centrifuge cascade having a uranium enrichment capacity equal to that of a gaseous diffusion plant would require over two million centrifuges, but the power requirement would be only 4% that of the gaseous diffusion process. Each of these centrifuges would be 100 cm long, have a radius of 10 cm, and revolve at 450 m/s. The two million centrifuges

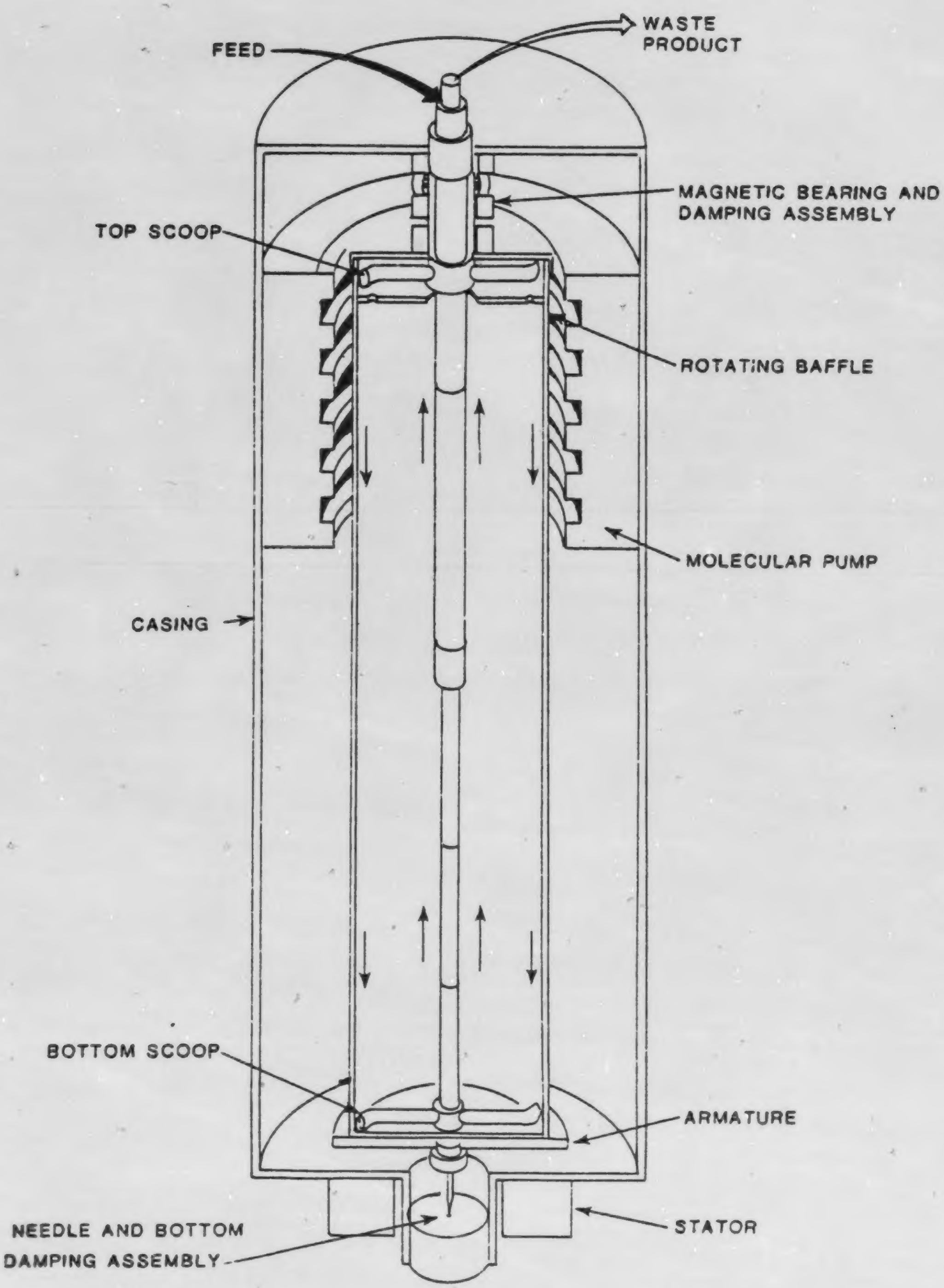

FEED
WASTE
PRODUCT
MAGNETIC BEARING AND
DAMPING ASSEMBLY
TOP SCOOP
ROTATING BAFFLE
MOLECULAR PUMP
CASING
BOTTOM SCOOP
ARMATURE
NEEDLE AND BOTTOM
DAMPING ASSEMBLY
STATOR

Figure 23-6-16. Early-model gas centrifuge.

would be divided into banks; numerous machines would be parallel in each bank; and about 23 banks would be connected in series.

The gas centrifuge process well may be the separation and enrichment technique of the future. Its relatively low power requirement gives it a distinct advantage over the gaseous diffusion proces. Table 23-6-1 compares the two processes and lists the advantages and disadvantages of each.

TABLE 23-6-1

SOME BASIC PROCESS DIFFERENCES BETWEEN THE GASEOUS DIFFUSION AND GAS CENTRIFUGE PROCESSES

Characteristic	Gaseous Diffusion	Gas Centrifuge
Enrichment of individual units	Low	High
Flow capabilities of individual units	High	Low
Process pressures	High	Low
Inventory in cascade	High	Low
Cooling requirements	Large	Small
Power usage	Large	Small
Lubrication requirements	Large	Essentially none
Projected equipment repairs and/or replacements	Small	Relatively large
Staffing requirements	Small	Relatively large

ELECTROMAGNETIC SEPARATION METHODS

Electromagnetic separation methods make use of magnetic and electronic forces in the manipulation of charged isotopic species. The oldest method for the separation of uranium isotopes, the Calutron electromagnetic method, was utilized during World War II by the Manhattan District of the Y-12 plant in Oak Ridge, Tennessee. Figure 23-6-17 is a schematic diagram of this process.

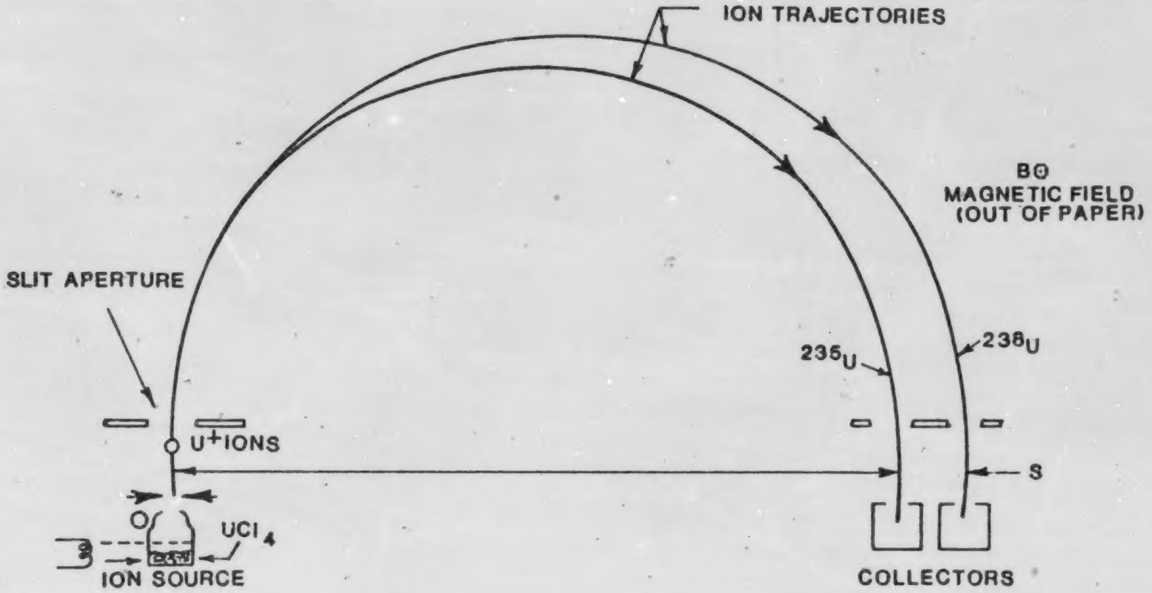

ION TRAJECTORIES
B⊙
MAGNETIC FIELD
(OUT OF PAPER)
SLIT APERTURE
^{235}U
^{238}U
U+IONS
S
O
UCl$_4$
ION SOURCE
COLLECTORS

Figure 23-6-17. Schematic diagram of electromagnetic isotope separation.

A salt feed material, typically uranium tetrachloride, is vaporized in an electrically-heated charge bottle. The vapor then passes through slots into an arch chamber, where the salt is ionized by an electron beam. The concurrently ionized uranium then passes through another slot, where it is accelerated by other electrodes into a vacuum tank and thus into the magnetic field of a large electromagnet.

Gaseous ions with isotopic differences but with the same kinetic energy have paths of different curvatures in a magnetic field. The magnet deflects the ions and, therefore, causes differences in the radii of the beam path of the ^{235}U ions and that of the ^{238}U ions, allowing these ions to be collected separately in reception pockets. The Oak Ridge isotope separation plant contained several very large magnets, each having a bank of calutrons, to obtain separated ^{235}U on a large scale. This method, however, is less efficient than gaseous diffusion for large-scale operation.

The plasma separation process is another electromagnetic method currently under development. This method is based upon the behavior of particles within a plasma in a constant magnetic field. A plasma is a gas in which a significant portion of its atoms or molecules exist in ionized form. These plasma ions, like any charged particle, can be manipulated by electric and magnetic fields. Since a charged particle of a given mass in a constant magnetic field travels at a mass-dependent frequency, additional energy imparted to the atom will cause it to move into a larger orbit. In the plasma separation process, energy can be imparted selectively by the electric field component of a radio frequency wave to the ^{235}U plasma ions. A strong magnetic field, or "bottle," confines the plasma by limiting the random motion of the uranium ions and electrons. The ions are geometrically separated and can be collected. Figure 23-6-18 depicts this process.

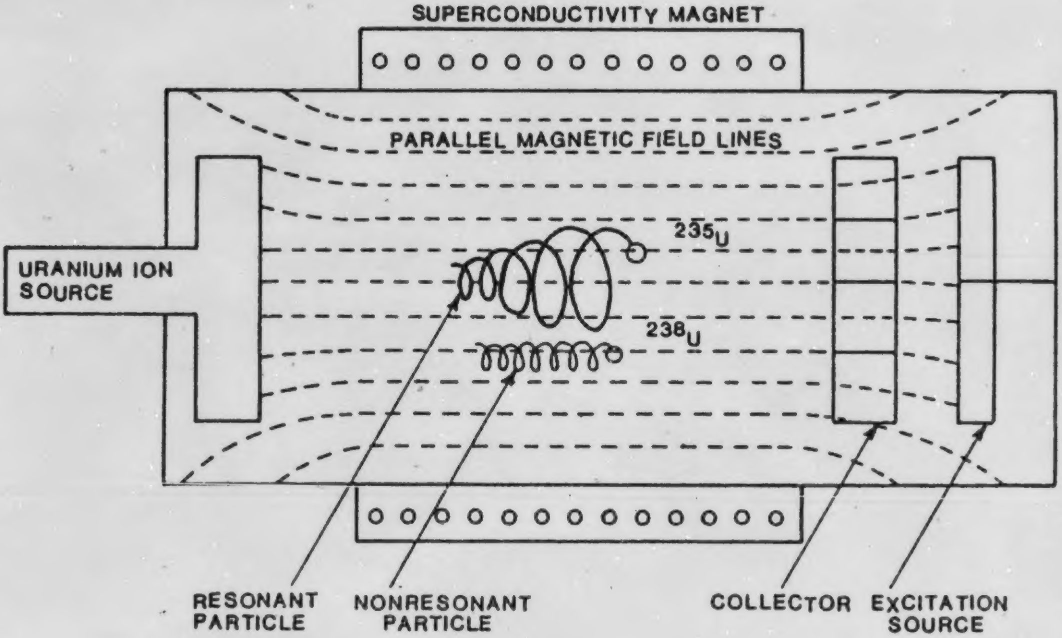

SUPERCONDUCTIVITY MAGNET
PARALLEL MAGNETIC FIELD LINES
URANIUM ION SOURCE
^{235}U
^{238}U
RESONANT PARTICLE
NONRESONANT PARTICLE
COLLECTOR
EXCITATION SOURCE

Figure 23-6-18. Plasma separation process.

LASER PROCESSES

Laser processes also make use of the selective excitation of a particular particle with a given nuclear mass. Lasers provide a light that has a sufficiently narrow frequency span to excite a particular isotope but not to excite the others. The object of laser isotope separation is to achieve the following criteria:

- Produce an isotopic species in such a form that one isotope selectively can absorb its resonant frequency.
- Find or tune a laser that emits that frequency.
- Use this light selectively to excite, or ionize, the desired isotope.
- Provide a means for removal of the desired specie from the undesired isotopes.

Various laser processes are being developed, and their implementation awaits the development of lasers of sufficient power to cause separation. These lasers should be available by the late 1980's.

EXERCISES

1. Describe the process used to convert yellowcake to UF_6. How does this process differ from uranyl nitrate conversion processes? What kind of equipment is used?
2. The "separation nozzle process" recently has been developed for uranium enrichment. Research this process, and write a report describing it.
3. Laser separation processes were not described in detail in this module. The molecular laser and the atomic vapor laser processes are two techniques currently under development. Research these processes, and prepare a report.

MATERIALS

None.

PROCEDURES

None.

DATA TABLES

None.

REFERENCE MATERIALS

Oak Ridge National Laboratory. ORNL/TM-5324 *A Guide to the Selection, Training, and Licensing or Certification of Reprocessing Plant Operators*, Volume II. Oak Ridge, TN: Oak Ridge National Laboratory, 1976.

Section I: Multiple Choice

Choose the best response(s) to the following questions.

1. The first step in the conversion of uranyl nitrate is its conversion to –
    a. Uranium dioxide.
    b. Uranium tetrachloride.
    c. Uranium trioxide.
    d. Uranyl phosphate.
2. A mechanical device for heating solids to elevated temperatures to change their chemical or physical properties by driving off vapors and gases is a –
    a. Distillation column.
    b. Calciner.
    c. Fluidized-bed reactor.
    d. Tower reactor column.
3. The reduction of uranium trioxide is accomplished in –
    a. Fluidized-bed reactors.
    b. Calciners.
    c. Cold traps.
    d. Distillation columns.
    e. Stirred-bed reactors.
4. Gaseous uranium hexafluoride is collected by passing it through a series of –
    a. Calciners.
    b. Cold traps.
    c. Distillation columns.
    d. Stirred-bed reactors.

5. Before uranium hexafluoride can be shipped, it must be converted from –
   a. A liquid to a gas.
   b. A gas to a liquid.
   c. A liquid to a solid.
   d. A gas directly to a solid.
6. Molecules of ^{235}U diffuse faster because they –
   a. Have a greater velocity (than ^{238}U ions).
   b. Are ligher than ^{238}U ions.
   c. Strike the barrier more frequently than ^{238}U ions.
   d. Have greater electrical attraction for the barrier.
7. The ideal point separation factor is –
   a. Theoretically possible.
   b. Smaller than the real point separation factor.
   c. Rarely achieved.
   d. Larger than the real point separation factor.
8. The ideal cascade –
   a. Is impossible to design.
   b. Is expensive to construct.
   c. Is one in which there is no mixing of streams of differing concentrations at the inlet to a separation stage.
   d. Provides an ideal separation factor.
9. The power requirement of the gas centrifuge process is –
   a. 50% that of the gaseous diffusion process.
   b. 4% that of the gaseous diffusion process.
   c. Greater than that of the gaseous diffusion process.
   d. About equal to that of the gaseous diffusion process.
10. Two electromagnetic separation processes are –
   a. The calutron process.
   b. Plasma separation process.

c. Separation nozzle process.

d. All of these.

Section II: Essay

11. Construct flowsheets that depict two processes for the conversion of uranyl nitrate to uranyl hexafluoride.

12. Draw a schematic of the gaseous diffusion process. Use the schematic to explain the process.

13. Write two equations that describe the ideal point separation factor of any isotope and the ideal point separation factor of ^{235}U and ^{238}U.

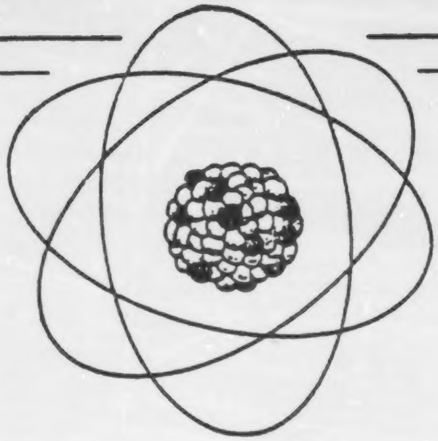
14. Why does the actual stage separation factor differ from the ideal point separation factor?

15. Describe the gas centrifuge process.

16. Define "diffusion cascade." Draw simple schematics (at least two) of typical cascade arrangements.

17. Describe two electromagnetic separation methods.

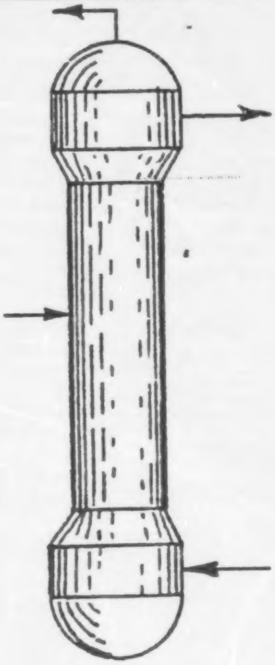
18. List four objectives of laser isotopic separation.



NUCLEAR TECHNOLOGY

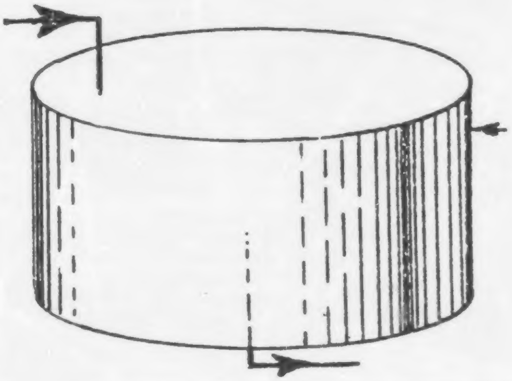
MODULE 23-7

NUCLEAR WASTE HANDLING PROCESSES



NUCLEAR CHEMICAL PROCESSES

COURSE 23



CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

COURSE MODULES

COURSE 23 NUCLEAR CHEMICAL PROCESSES

MODULE 23-1	Head-End Treatment
MODULE 23-2	Ion Exchange
MODULE 23-3	Solvent Extraction
MODULE 23-4	Precipitation Techniques and Centrifugation
MODULE 23-5	Techniques of Chemical Concentration
MODULE 23-6	Diffusion and Enrichment Process
⇨ MODULE 23-7	Nuclear Waste Handling Processes

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INTRODUCTION

Nuclear energy is providing roughly one-eighth of the power generated in this country. In 1978, the nuclear energy industry produced nearly 300 billion kilowatt hours of electricity. However, as with any industry, the process of generating electric power by nuclear methods produces substantial quantities of wastes. These wastes are unique, in that they contain nuclides that remain radioactive for thousands of years. Clearly, nuclear waste management has one of the most significant overall functions in the field of nuclear technology — that of reprocessing, treating, and storing radioactive waste materials.

The purpose of this module is to examine the types and characteristics of nuclear wastes, the major handling procedures that the wastes undergo, and the problems of containing the energy and radioactive materials. The purpose of nuclear waste management is to provide reasonable assurance that radionuclides will be isolated from the biosphere until they have decayed to the point that the residual risks are acceptably low.

MODULE PREREQUISITES

The student should have completed a course in basic algebra; Course 2, "Radiation Protection I"; Course 11, "Radiation Detection and Measurement"; Course 17, "Radiation Protection II"; and Course 20, "Radiation Monitoring Techniques."

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define the following terms:
    - Low-level waste.
    - Intermediate-level waste.
    - High-level waste.
    - Calcination.
    - Evaporation.
    - Ion exchange.
    - Batch and column method.
    - Relative hazard index (RHI).
    - Maximum permissible concentration (MPC).
    - Decontamination factors.
2. Explain the purpose of nuclear waste handling.
3. Give the title of the document in which the acceptable levels of nuclear waste may be found.
4. List and describe the three types of nuclear waste (in terms of physical phase) and the major type of handling procedure associated with each.
5. List three radioactive solids and three radioactive liquids commonly encountered in nuclear waste management.
6. Describe in detail one major type of waste handling process.
7. List three safety design features associated with nuclear waste management.
8. Calculate relative hazard index and decontamination factors, given sufficient data concerning the index and contamination.
9. Describe three proposed methods of waste storage.

The purpose of nuclear waste management, as defined by the U.S. Department of Energy (DOE), is to —

> manage radioactive wastes in such a manner as to minimize the radiation exposure and associated risk to man and his environment over the lifetime of the radionuclides ... to control potential sources of pollution as far below established standards as practical, considering both technology and economics. (ERDA Manual, Chapter 0511, "Radioactive Waste Management").

Acceptable levels of radioactive material in air and water have been defined under Federal law in the Code of Federal Regulations, Title 10, Part 20 (10 CFR 20). Levels above these volumes are considered potential health risks.

The time of confinement of nuclear wastes depends primarily upon the half-lives of the specific radionuclides and upon their concentrations in the wastes. Methods are employed in waste handling to reduce the volume of waste streams and, at the same time, to convert them to convenient forms physically and chemically acceptable for storage.

A nuclear fuel does not possess an unlimited life. The amount and type of nuclear fuel present in a reactor and, therefore, the resulting waste material produced, will vary according to the relationship of the reactor type, neutron activation of the coolant and its impurities, the corrosion and wear products from the cladding and core structures, the power level, and the operating schedule of the reactor.

Radioactive wastes may be categorized as either solids, liquids, or gases. The three waste forms are further classified as being combustible (capable of being easily set on fire) or noncombustible (not easily inflamed) and as being a low-, intermediate-, or high-level waste, according to radioactivity level and thermal output.

The definitions of low-, intermediate-, and high-level wastes are far from being standardized. They have different connotations for different individuals. For example, a waste that is "high level" to a research reactor operator may be "low level" to a chemical reprocessor. For purposes of this module, low-level wastes are considered to be those that may be handled directly and that require no special precautions. Intermediate- and high-level wastes are referred to as those that cannot be handled directly or without special shielding. High- and low-level wastes are expressed quantitatively in Table 23-7-1.

TABLE 23-7-1.
QUANTITATIVE DEFINITIONS FOR HIGH AND LOW ACTIVITY LEVELS.

Physical State	Class	Concentrations
All	Unrestricted	Background to 0.1 of limits in 10 CFR Part 20
	Low	0.1 of limits in 10 CFR Part 20 to 10^{-4} μCi/cm^3.
	High	10^{-4} μCi/cm^3.
Liquid	Low	0.1 of limits in 10 CFR Part 20 to 10^{-2} μCi/cm^3.
	High	10^{-2} μCi/cm^3.
Solid	Low	0.1 of limits in 10 CFR Part 20 - 50 mr/hr at contact or 10^3 μCi of alpha material per container
	High	All solid wastes above 50 mr/hr at contact or containing over 10^3 μCi of alpha material per container

Low-level wastes are not as "hot" radioactively or thermally as high-level wastes. They originate outside the reactor and include materials contaminated secondhand and are not directly concerned with the nuclear process. These materials include clothing, gloves, containers, tools, machinery, and mine tailings. After collection, low-level solid wastes usually are compacted to reduce their volume and then are packaged in boxes or metal drums for transport to a disposal site, where they either are buried or incinerated.

Intermediate-level wastes have an average activity concentration of a few hundredths of a curie per gallon. The liquid wastes are routinely neutralized with sodium hydroxide, which precipitates out the insoluble constituents of the waste solution. The remaining liquid (supernate) is concentrated by evaporation. The predominant radionuclides in intermediate-level wastes are cesium-137 (about 1 Ci/gal) and strontium-90.

High-level wastes usually are found in smaller volumes than low-level wastes. They originate from used fuel rods and a reprocessing procedure which reclaims any unused plutonium and uranium for reuse in light water reactors. In the reprocessing of used fuel rods, a solvent strips out the fissionable material, leaving behind corrosive liquid wastes consisting of cesium-137, strontium-90, iodine-131, and other radionuclides.

Most of the high-level wastes are generated as liquids, usually in the form of sludge or salt cake. The sludge is precipitated out of the liquid, and the salt cake results from a partial evaporation of the liquid. This in turn results in about a 3.5 to 1 volume reduction. Both the sludge and the salt cake are relatively soluble. The major nuclide in the sludge is strontium-90, and in the salt cake, cesium-137.

The chemical and radionuclide composition of the waste changes as the waste ages. The major changes are (1) radiolytic decomposition of the waste, (2) the decay of radionuclides, and (3) the partitioning of the waste into sludge and supernate. The salt formed by evaporation of the supernate consists of $NaNO_3$, $NaOH$, Na_2CO_3, $NaNO_2$, Na_2SO_4, and $NaAl(OH)_4$. The radionuclide concentration in the salt is approximately three times that of the supernate.

Another category of high-level waste consists of the transuranics. They have atomic numbers higher than uranium (at 92) on the periodic table of elements. Their extremely long half-lives complicate waste disposal because techniques for long-term storage must be utilized. These transuranics include neptunium, plutonium, americium, and curium. Transuranic wastes are those known to contain more than ten nanocuries of alpha emitters per gram of waste.

Waste treatment and fixation methods naturally take into account the different physical phases (solid, liquid, and gas) and characteristics of waste stream. The particular handling process employed for a given waste usually depends upon the type and classification of the waste. Figure 23-7-1 is a schematic diagram of the general disposal techniques frequently employed.

Evidence of the magnitude of the nuclear waste management process is given in Table 23-7-2, which indicates the volumes and activity levels from the light-water fuel cycle. Most U.S. reactors are light-water-cooled: these include research, test, plutonium production, power, and propulsion reactors.

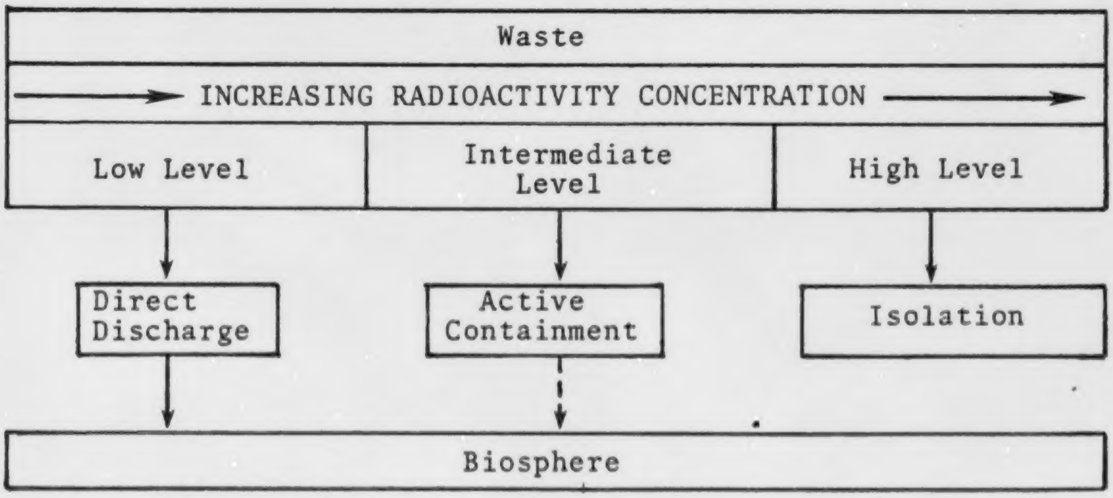
Waste
INCREASING RADIOACTIVITY CONCENTRATION
Low Level
Intermediate Level
High Level
Direct Discharge
Active Containment
Isolation
Biosphere

Figure 23-7-1. Schematic diagram of general disposal techniques.

TABLE 23-7-2.
VOLUMES AND ACTIVITY LEVELS FROM LIGHT-WATER REACTOR CYCLE.

Type of Waste	Volume (m^3)	Activity (mCi)
High-level solidified	3.0	78
Cladding hulls	2.61	0.87
Noble gases	0.1	0.27
Iodine	0.043	1.1×10^{-6}
LWR tritium (water)	140	0.00074
Fission-product tritium	0.31	0.016
Carbon-14	---	2×10^{-5}
Low-level transuranic	3.5	0.0035
Intermediate-level transuranic	8.7	0.011
Nontransuranic	535	0.002
Ore tailings	57,000	0.0006

WASTE REPROCESSING

Waste reprocessing, typically known as the "back end" of the fuel cycle, refers to the treatment of nuclear fuel after it is removed from the reactor. Its relationship to the entire fuel cycle is given in Figure 23-7-2.

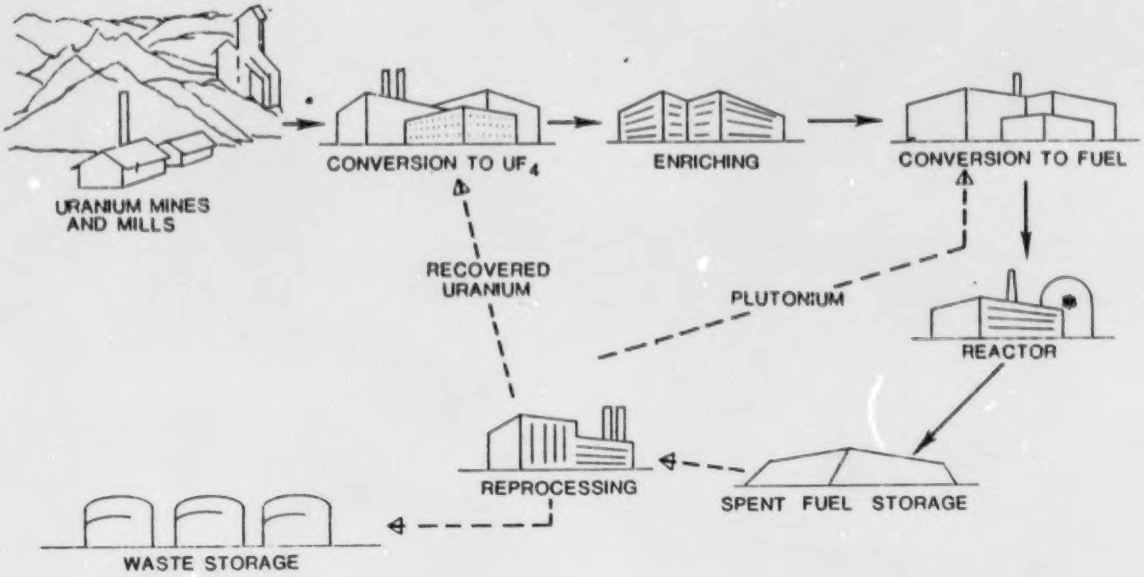
URANIUM MINES AND MILLS
CONVERSION TO UF4
ENRICHING
CONVERSION TO FUEL
RECOVERED URANIUM
PLUTONIUM
REACTOR
REPROCESSING
SPENT FUEL STORAGE
WASTE STORAGE

Figure 23-7-2. The light-water-reactor fuel cycle.

A synopsis of the fuel reprocessing cycle will be helpful, as it is responsible for most of the nuclear waste produced. Once a year, about one-third of the nuclear fuel in a reactor – roughly thirty metric tons – is replaced. After removal, the spent fuel customarily is sent to a chemical reprocessing plant. (However, at this time – June, 1980 – commercial reprocessing has been discontinued until further studies have been completed.)

Fuel reprocessing is a recycling technique that not only extends the United States' supply of uranium-235, but reduces the volume of nuclear waste that must be stored.

The recycling process consists of the following main steps:

1. Separation of plutonium and uranium by organic solvent extraction and the conversion of plutonium to plutonium oxide and uranium-235 to uranium oxide.
2. The two oxides then are combined to make a mixed oxide fuel and are formed into fuel elements for use in reactors.

The process is required to recover greater than 95 percent of the unconsumed uranium and to reduce the fission product activity to a level that will allow further processing without shielding. The reprocessing cycle is depicted in Figure 23-7-3.

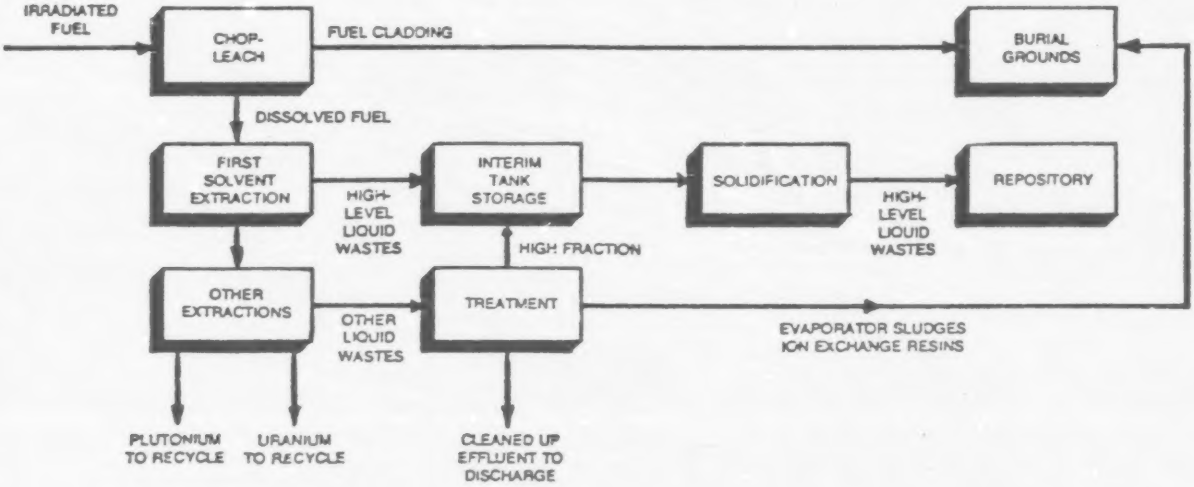
IRRADIATED FUEL
CHOP-LEACH
FUEL CLADDING
BURIAL GROUNDS
DISSOLVED FUEL
FIRST SOLVENT EXTRACTION
HIGH-LEVEL LIQUID WASTES
INTERIM TANK STORAGE
SOLIDIFICATION
HIGH-LEVEL LIQUID WASTES
REPOSITORY
HIGH FRACTION
OTHER EXTRACTIONS
OTHER LIQUID WASTES
TREATMENT
EVAPORATOR SLUDGES
ION EXCHANGE RESINS
PLUTONIUM TO RECYCLE
URANIUM TO RECYCLE
CLEANED UP EFFLUENT TO DISCHARGE

Figure 23-7-3. The reprocessing cycle.

During the operation, wastes of various levels of radioactivity are generated, including intermediate-level liquid waste (ILLW) and high-level liquid waste (HLLW). They originate from:

- Reagents added during the chemical process.
- Products arising from corrosion to the plant, material (impurities) present in the fuel element and not removed in the process, and reactor fuel incompletely removed.

The origins and types of wastes are explained in Figure 23-7-4, and Table 23-7-3 lists many of the important fission products involved in chemical reprocessing.

ILLW originate from the secondary extraction steps and contain fission products and transuranics.

HLLW are long-lived in terms of radioactivity and contain from 0.1 percent to 0.2 percent of the plutonium and uranium of the spent fuel. These wastes are highly corrosive and possess sufficient decay heat to cause boiling.

Federal regulations state that the wastes should be stored in containers for at least five years to allow for radioactive decay. Then the wastes undergo calcination, a process in which the wastes are solidified into a mixture of powder and granules. This procedure is to be followed by vitrification, incorporation of the calcined particles in a stable matrix such as glass. The solidified product should be a chemically stable solid that will not revert to a liquid or a gas in the presence of high radiation or temperature.

Low-level and intermediate-level liquid waste treatment methods include ion exchange and evaporation. Treatment methods will be discussed individually, according to

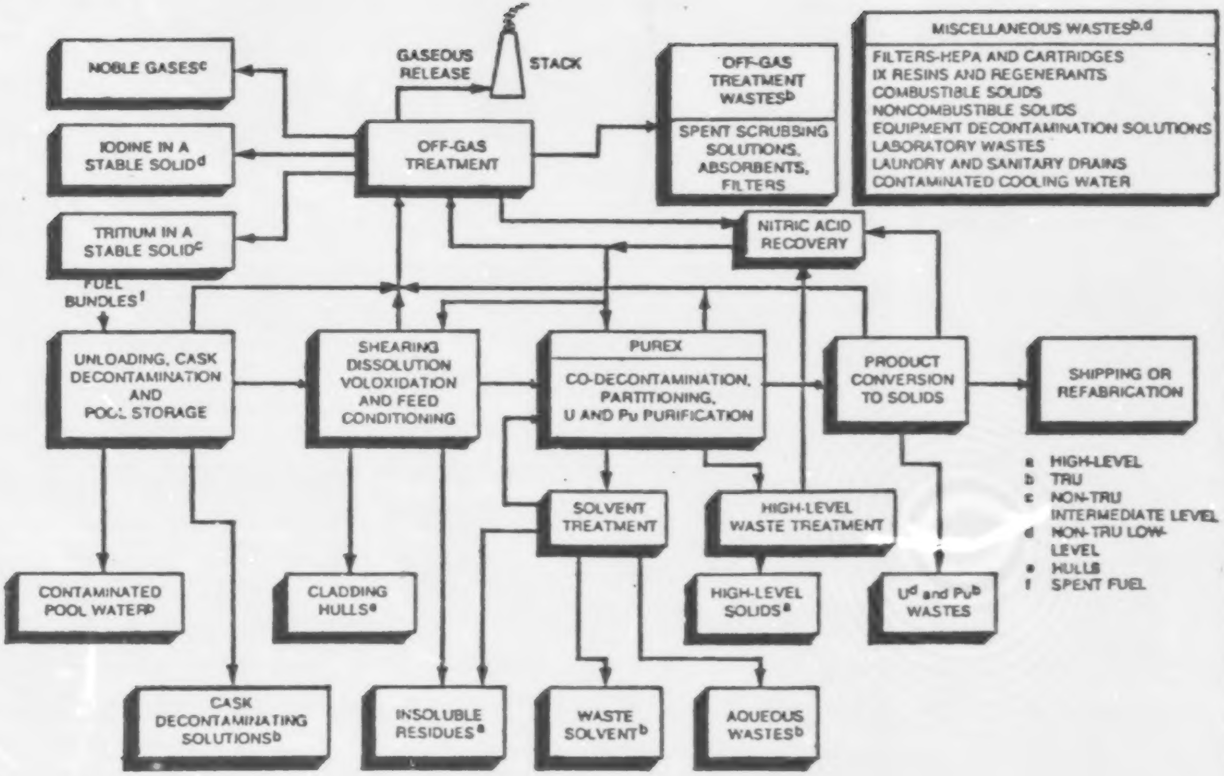
NOBLE GASES[c]
IODINE IN A STABLE SOLID[d]
TRITIUM IN A STABLE SOLID[c]
GASEOUS RELEASE
STACK
OFF-GAS TREATMENT
OFF-GAS TREATMENT WASTES[b]
SPENT SCRUBBING SOLUTIONS, ABSORBENTS, FILTERS
MISCELLANEOUS WASTES[b,d]
FILTERS-HEPA AND CARTRIDGES
IX RESINS AND REGENERANTS
COMBUSTIBLE SOLIDS
NONCOMBUSTIBLE SOLIDS
EQUIPMENT DECONTAMINATION SOLUTIONS
LABORATORY WASTES
LAUNDRY AND SANITARY DRAINS
CONTAMINATED COOLING WATER
NITRIC ACID RECOVERY
FUEL BUNDLES[f]
UNLOADING, CASK DECONTAMINATION AND POOL STORAGE
SHEARING DISSOLUTION VOLOXIDATION AND FEED CONDITIONING
PUREX
CO-DECONTAMINATION, PARTITIONING, U AND Pu PURIFICATION
PRODUCT CONVERSION TO SOLIDS
SHIPPING OR REFABRICATION
SOLVENT TREATMENT
HIGH-LEVEL WASTE TREATMENT
CONTAMINATED POOL WATER[b]
CLADDING HULLS[e]
HIGH-LEVEL SOLIDS[a]
U[d] and Pu[b] WASTES
CASK DECONTAMINATING SOLUTIONS[b]
INSOLUBLE RESIDUES[a]
WASTE SOLVENT[b]
AQUEOUS WASTES[b]
a HIGH-LEVEL
b TRU
c NON-TRU INTERMEDIATE LEVEL
d NON-TRU LOW-LEVEL
e HULLS
f SPENT FUEL

Figure 23-7-4. The origins of wastes in the nuclear fuel cycle.

TABLE 23-7-3.

COMMON FISSION PRODUCTS INVOLVED IN CHEMICAL REPROCESSING.

Fission Product	Fission yield, percent*	Half-life	Radio-activity
Ru^{103}...........	3.0	45 days	β β
Ru^{106}-Rh^{106}†....	0.5	290 days	γ β β γ
Zr^{95}-Nb^{95}†......	6.2	65 days	γ γ β β γ
Nb^{95}............	6.2	38.7 days	γ γ β
Ce^{141}...........	6.1	28 days	γ β
Ce^{144}-Pr^{144}†....	5.2	275 days	γ β β β
Kr^{85}............	0.33	9.7 years	γ γ β
Sr^{89}............	4.7	54 days	β
Sr^{90}-Y^{90}†.......	5.2	25 years	β
Y^{91}.............	5.6	57 days	β β
TE^{129}-Te^{129}†....	0.4	32 days	β γ
Cs^{137}-Ba^{137}.....	6.1	33 years	γ γ β β
BA^{140}...........	6.2	12.8 days	γ β β
La^{140}†..........	6.2	40 years	γ β β β
Pr^{143}...........	5.6	13.8 days	γ γ γ β
Nd^{147}...........	3.0	11.8 days	β β
Pu^{147}...........	3.0	3.7 years	γ β
All other radioactive fission products...........			β γ
Total			β + γ

*These numbers are based on the assumption that no radioactivity has been removed from the feed by volatization of ruthenium or by scavenging of zirconium and niobium (i.e., by the "bend-end" treatments).

†Quantity of emitted radioactivity is governed by decay of long-lived parent.

chemical phase, to allow a more thorough understanding of the processes involved.

LIQUID WASTE MANAGEMENT

CALCINATION

The original process of calcination was developed for the solidification of high-level waste from the processing of aluminum clad test reactor fuel. It has been modified to calcine fluoride bearing zirconium waste, stainless steel sulfate waste, and ammonium nitrate containing waste. The process converts liquid waste to granules of a size from 0.05 to 0.5 mm (0.002-0.02 in). A flowsheet of a typical waste calcining facility is provided in Figure 23-7-5. There are different designs for calcining facilities, although most of the designs incorporate the same fundamental techniques.

In the calciner, the liquid waste is reduced to a fine spray by air pressure from three nozzles at 85-140 gph and blown into a heated fluidized bed of solidified granular waste at a temperature of 400-500°C. The process begins with dolomite as the solidified granular material; dolomite is replaced by calcine as the operation continues.

The bed is heated by an in-bed combustion of an oxygen and atomized kerosene stream. At temperatures of 360-400°C, the atomized kerosene will ignite in the presence of a nitrate waste.

The purpose of much of the equipment in Figure 23-7-5 is to clean up radioactive particles in the gases produced by the calcination process. The off-gases pass through a

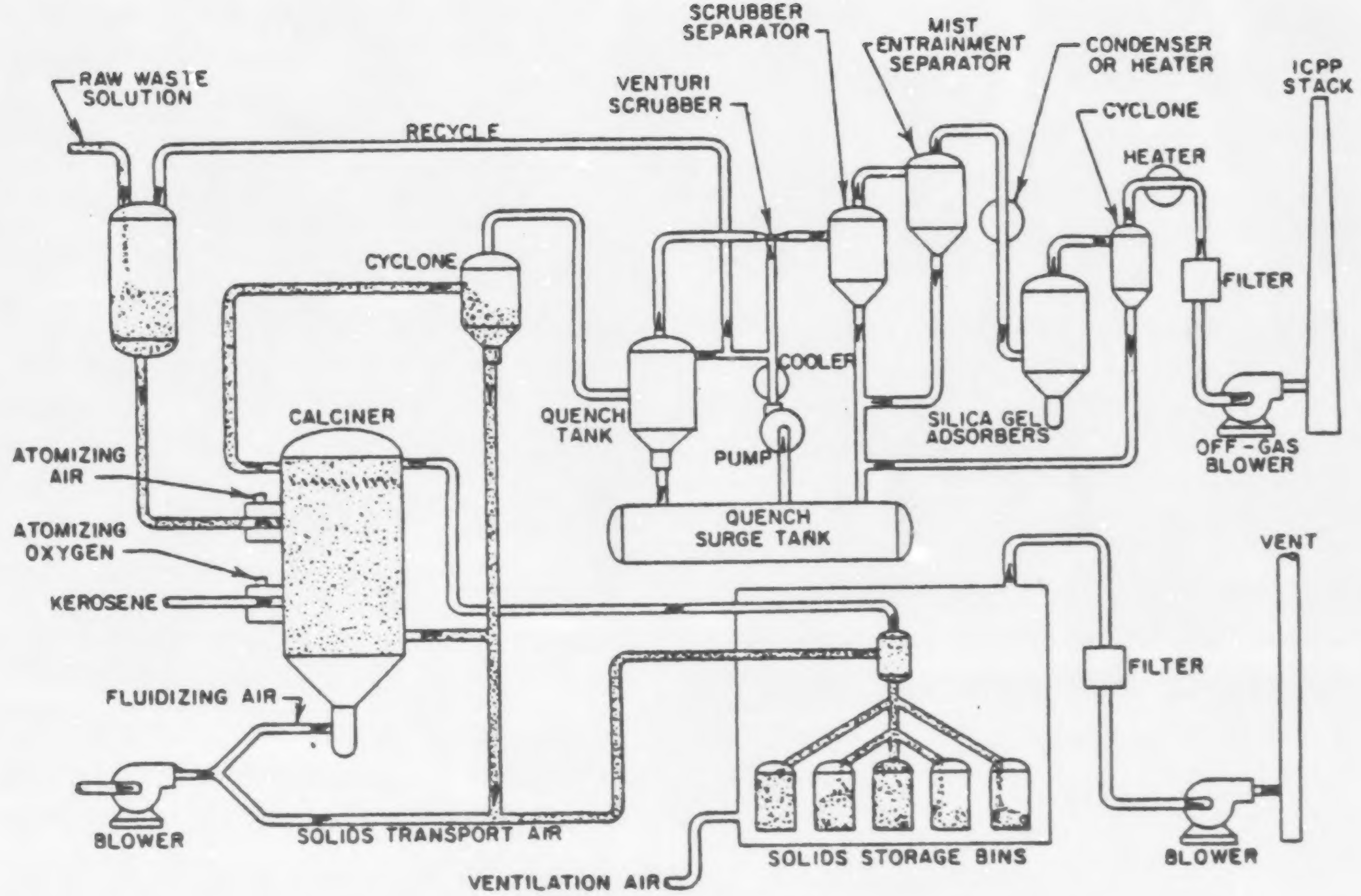
RAW WASTE SOLUTION
RECYCLE
SCRUBBER SEPARATOR
MIST ENTRAINMENT SEPARATOR
CONDENSER OR HEATER
ICPP STACK
VENTURI SCRUBBER
CYCLONE
HEATER
CYCLONE
FILTER
COOLER
QUENCH TANK
PUMP
SILICA GEL ADSORBERS
OFF-GAS BLOWER
CALCINER
ATOMIZING AIR
ATOMIZING OXYGEN
KEROSENE
QUENCH SURGE TANK
VENT
FILTER
FLUIDIZING AIR
BLOWER
SOLIDS TRANSPORT AIR
SOLIDS STORAGE BINS
BLOWER
VENTILATION AIR

Figure 23-7-5. A typical waste calcining facility.

cyclone to remove most of the solids, a quench tank (condenser) to cool the gas, a venturi-scrubber, demister, a silica gel adsorber for the removal of volatile ruthenium, another cyclone, and a high-efficiency particulate filter (HEPA) to remove submicron particles before discharge through a plant stack 250 feet in height.

Nitric acid and water are utilized to dissolve any particles of calcine that may have been deposited in the off-gas scrubbing system. The acid-water solution is recycled at 15-30 gph through the calciner feed and is 20-30 percent of the total supply to the calciner.

Some of the physical, chemical, and radiochemical properties of calcined solids from acid aluminum waste and fluoride bearing zirconium waste are listed in Table 23-7-4.

TABLE 23-7-4.

TYPICAL PROPERTIES OF CALCINER PRODUCT.

Physical Properties	Aluminum Waste	Zirconium Waste
Mass median particle diameter, mm	0.56-0.70	0.6-0.8
Bulk density, g/cc	1.0 -1.2	1.7
Composition (wt %)		
Zirconium as ZrO_2	--	21.4
Calcium as CaF_2	--	54.2
Aluminum as Al_2O_3	88.2-89.1	21.9
Sodium as Na_2O	1.3- 2.0	--
Nitrogen as N_2O_5	3.9- 4.1	1.9
Mercury as HgO	2.9	--
Water	2.0	0.6
Gross fission product oxides	0.6	--
Radioactive properties		
Heat generation, Btu/hr-lb	0.3-0.8	0.1-0.2
Principal radioisotopes, Ci/lb		
Strontium-90	4.9-7.2	0.8-2.5
Cesium-134	0.2-0.4	--
Cesium-137	5.2-8.0	1.0-3.0
Cesium-144	1.3-17.3	--
Ruthenium-106	0.04-0.5	0.01-0.03
Zirconium/niobium-95	0-0.5	--
Promethium-147	3.3-10.6	--

After calcination, the granules will be vitrified, fused with borosilicate glass, and then placed into stainless steel canisters for storage.

For each ton of spent reactor fuel processed, high-level liquid wastes will be concentrated to approximately 100-400 gallons and then converted to between two and three cubic feet of solidified waste. After two years of cooling, the waste will contain approximately 300,000 curies of fission-product activity, producing 4,000 Btu per hour (1,000 watts) of heat output, and may contain up to 59 grams of plutonium.

Storage in canisters is a highly leach-resistant method of waste disposal. Leaching occurs when a waste material is subjected to the action of water or other liquid that removes or separates the soluble components. Proper storage methods are important to prevent leached contaminants from entering the water table.

LOW AND INTERMEDIATE LEVELS OF LIQUID WASTE HANDLING

Low and intermediate levels of radioactive waste — by virtue of their activity, radiotoxicology, or form — are considered to be disposable on, or near, the surface of the earth after minimal decontamination treatment. Such treatment entails evaporation or ion-exchange techniques.

Evaporation

In an evaporator, the liquids are converted into a vapor, leaving behind insoluble particulates. Evaporation gives a decontamination factor higher than that required for many reactor applications. For this reason, many reactor systems include evaporators to provide an extra safety factor. Decontamination factors may range from 10^3 to 10^8, as seen in Table 23-7-5.

TABLE 23-7-5.
A COMPARISON OF EVAPORATORS.

Installation	Knolls	Oak Ridge	Brookhaven	Argonne	Mound
Capacity of equipment	400 gal/hr (0.42 l/sec)	285 gal/hr (0.30 l/sec)	600 gal/hr (0.63 l/sec)	150 gal/hr (0.158 l/sec)	100 gal/hr (0.105 l/sec)
Type of equipment	Forced-feed flash	Pot-type removable heating coils	Vapor compression	Vertical tube circulation	1st effect-vertical tube forced-feed
De-entrainment device	baffled separating column	cyclone-type separator	vapor dome, fiberglas bed	centrifugal separator, centrifix scrubber, (reflux if necessary)	2nd effect-vertical tube natural circulation
Typical feed (average activity)	$3 \cdot 10^{-2}$ μc/cm^3	(β) $2 \cdot 10^{-2}$ μc/cm^3	$1 \cdot 10^{-2}$ μc/cm^3	(α + β) 10^{-3} μc/cml	(β) 10^{-4} μc/cm^3
Typical feed (average solids)	0.3%	8.0%	0.5%	0.2%	3.0%
Overall decontamination factor	10^4-10^5	10^{3+}	10^6-10^7	10^4-10^5	~10^8
Volume reduction factor	400	15	110	100	32
Slurry (average solids)	70%	70%	63%	20%	60%
Steam efficiency	85%	70%	100%	85%	92.5%

Several evaporator systems have been designed for various applications; for example, a forced-circulation evaporator with an external heating surface, a natural circulation evaporator with an external heating surface, a coil evaporator, and a double-effect evaporator. All types operate reasonably well for the concentration of solutions that contain radioactive material, and they provide the extra benefit of being relatively inexpensive.

One of the greatest technical problems associated with evaporators is in regard to the suspension of radioactive contaminants in the vapor. Various methods have been employed to prevent these suspensions; such methods include the use of centrifugal separators, filtration, and reflux.

Foaming also is a problem in the evaporator and must be controlled because it may result in poor decontamination results. Antifoam agents, baffles, and pH controls have been employed in the control of foaming.

Ion Exchange

Ion exchange is a reversible exchange of ions between a solid and a liquid, but in which there is no substantial change in the structure of the solid. The fission products commonly subjected to the ion-exchange process are cesium-137, strontium-90, and plutonium-238 and -239.

In nuclear waste treatment, the "solid" is the ion-exchange material, a resin particle. A resin is a high-molecular-weight polymer that contains particular ionic groupings as a basic part of the structure. (A polymer is a compound of large molecules formed by the repetitious union of many small molecules.)

The four major types of ion-exchange resins in use today are strongly and weakly acidic resins (cation resins), and strongly or weakly basic resins (anions resins).

Cation resins contain phenolic, sulfonic, carboxylic, or phosphoric acid groups with equal amounts of mobile sodium or hydrogen ions.

Anion exchangers contain amine groups attached to mobile ions such as chloride or hydroxyl ions. The mobile ions on both the anion and cation resins are exchanged for other ions of the same sign (electrical charge) in the waste material. The extent to which the exchange takes place is limited by the selectivity of the resin.

A modificiation of the structure of the resin, known as "crosslinkage," varies its chemical and physical properties. Crosslinkage binds a linear polymer chain in the resin with another substance, which produces a three-dimensional insoluble copolymer. Crosslinkage is indicated by an X following the name of the particular resin; for example, Dowex 50-X8.

The two methods of exposing the nuclear liquid wastes to the resins are known as the "batch method" and the "column method." (The column method may be described further with regard to whether or not the resin bed is fixed or moving and whether or not the waste solution and cleansed solution flow past the resin in the same relative direction or in opposite directions.)

Batch Method

In the batch method, the resin and solution are mixed together in a tank and allowed to come to equilibrium. Equilibrium is reached when all the mobile ions of the resin have taken the place of the ions in the waste solution.

The solution then is filtered off and the resin prepared for the next cycle.

Column Method

A column operation usually consists of a vertical cylinder filled with an ion-exchange resin. The resin is supported by some type of filter base, such as gravel; and the waste solution is fed through the column.

A solution can be deionized almost totally with a cation and anion bed. The resins also may be mixed together to form a mixed bed.

As ionization proceeds, the upper layers of the resin column are completely converted to the form that contains the ions in the waste solution. They are "exhausted," and no further exchange will take place. The location of exchange eventually will reach the bottom of the column, and the exchanging ions in the waste solution will show up in the effluent. This is known as "breakthrough." The process usually is discontinued before breakthrough and the column "regenerated" by reversal of the exchange process.

The resin is treated with a concentrated solution containing the original mobile ion to accomplish regeneration. Regeneration solutions usually are 6N HCl and 4% NaOH. (N refers to "normality," the number of equivalent weights of HCl per liter of solution.)

It is sometimes more practical to dispose of the exhausted resin than to reuse it. The resin is mixed with Portland Cement, allowed to solidify, and disposed of in this form.

The removal of radioactivity by ion exchange is affected by crosslinkage, resin particle size, feed flow rate, pH, resin bed composition, bed depth, and temperature.

Most of the applications of ion-exchange resins to the treatment of reactor wastes involve activity levels at which the effect of radiation upon the resin is very slight. Adsorption is affected by differing amounts in regard to commercially available resins when higher levels of radiation are involved.

SOLID WASTE MANAGEMENT

The largest volume of solid contaminated waste involves low-level "trash," including such items as cleaning rags, tools, and equipment. The amounts generated vary according to reactor type and size; but as a general rule, from 1,000 to 5,000 ft^3/yr (30 to 140 m^3/yr) are produced.

Smaller volumes of wastes, such as spent resins from ion-exchange systems, evaporator pans, incinerator ash, control rods, etc., contain considerably higher levels of radioactivity.

In the handling of solid wastes, the materials frequently are first separated in terms of activity level and combustibility. Low-level wastes are handled directly, and ordinarily require no particular safeguards. The high-level wastes, such as spent ion-exchange resins, however, either must be flushed into storage tanks to decay or placed, by mechanical devices, into shielded containers, for handling.

Hardware taken from within the reactor must be appropriately shielded, depending upon the size, shape, and radioactivity level of the material.

Fuel assemblies are removed from reactors by mechanical handling techniques and stored in liquid coolant, such as water, for several months to allow for the decay of the short-lived fission products. This "cooling" period often is provided for many of the high-level solid wastes to reduce the amount of shielding necessary and to lower the cost of handling and shipping. Under current U.S. regulations, spent fuel elements must be cooled 90 days before shipping, in order to reduce heat production and to allow the iodine-131 content to decay to an acceptable level.

Incineration is generally used for low-level combustible trash because the total volume can be reduced by as much as 95 percent and the weight by possibly 70 percent. The off-gases produced during incineration are processed and a high degree of decontamination achieved.

Low-level trash also can be baled to reduce the volume and is less expensive than incineration.

Those low-level wastes that are not incinerated or baled are buried under the guidelines of 10 CFR 20. Those wastes that are shipped to a certain location for burial are sent in steel barrels, in boxes of various materials, and in concrete.

Large pieces of contaminated equipment often are secured in a fenced open field, where the equipment is monitored and is allowed to decay for several years.

GASEOUS WASTE MANAGEMENT

The actual volumes of true radioactive gases are relatively small, and the quantity of radioactive material is reduced to a negligible quantity.

A gaseous waste system is designed to store and treat the small volumes of highly active off-gases, to filter vent gases from fuel areas and the liquid and solid waste processing equipment, to monitor all gas streams, and to discharge the gases through stacks of varying heights (from 100 to 400 ft).

Gas transport systems (ducting, etc.) must be leak-proof and corrosion resistant. As a safeguard, each area within a nuclear facility is designated as a hazard area on a scale that ranges from low to high. Control rooms are under the highest pressure, and waste processing areas have the lowest pressure.

Gaseous wastes may be cleansed, stored, "scrubbed" (cleansed with liquids to precipitate or dissolve particulates), passed over activated charcoal at below freezing temperatures to remove organic compounds of high molecular weight, and filtered to remove particulate matter.

Gases also are stored for decay: They are cooled to remove water vapor and stored in iron tanks. The size of the storage system is determined by the decay periods for the nuclides. These periods may vary from 120 days to only a few minutes. The estimated gaseous effluent activity is listed in Table 23-7-6.

Hydrogen, an explosive gas, is reduced by use of a catalytic recombiner or diluted and released through the stack. Release stacks are designed to allow maximum mixing with the outside air and are built for exit velocities of from 50 to 80 ft/sec. The stack height is a function of its geographical and structural location and general atmospheric conditions. Rapid mixing is desirable, and dilution factors of from 10^3 to 10^5 normally are expected.

TABLE 23-7-6.
ESTIMATED GASEOUS EFFLUENT ACTIVITY.

		Release rate (microcuries*/sec)[1]		
Nuclide	Half-life	30 min. delay[2]	1 day delay[3]	60 day delay[4]
^{83m}Kr	1.86 hr.	3,600	0.5	0
^{85}Kr	10.76 yr.	10	10	10
^{85m}Kr	4.4 hr.	6,400	156	0
^{87}Kr	1.3 hr.	19,200	0.06	0
^{88}Kr	2.8 hr.	20,400	60	0
^{89}Kr	3.2 min.	440	0	0
Total Kr activity (microcuries/sec)		50,000(approx.)	226	10
			15 day decay[3]	
^{131m}Xe	11.9 day	15	6	0.4
^{133}Xe	5.27 day	6,400	880	2
^{133m}Xe	2.3 day	240	2	0
^{135}Xe	9.2 hr	21,600	0	0
^{135m}Xe	15.6 min.	10,400	0	0
^{137}Xe	3.8 min.	1,120	0	0
^{138}Xe	14 min.	31,200	0	0
Total Xe activity		72,000(approx.)	888	2.4
Total Xe and Kr Activity (microcuries/sec)		122,000	1,100	12
Total Xe and Kr Activity (curies/yr)		3,000,000	27,500	300

[1] Assumes operation with 0.2% clad defects.

[2] Typical hold-up time in BWRs built to date.

[3] Typical hold-up time for BWRs using charcoal beds.

[4] Typical hold-up time in PWRs.

* microcurie = 10^{-6} curie = 0.000001 curie.

The most frequently used filters are 24 x 24 x 12 in (61 x 61 x 30.5 cm) and are designed to handle from 800 to 1,000 ft^3/min. When properly installed, the filters should stop particulates in the size range of approximately 0.3 microns. A high-efficiency particulate filter (HEPA) is greater than 99.95 percent efficient.

A gaseous system is closely monitored in order that the levels of radioactive wastes in disposal areas can be determined. Instruments measure individual pipes and storage tanks, waste streams going into the stack, waste streams coming out of the stack, and point locations around the management facility. Gas streams normally are not mixed until they have been monitored.

The monitors measure particular isotopes; alpha, beta, and gamma radiation; and particulate matter.

SAFETY ASPECTS OF NUCLEAR WASTE MANAGEMENT

Safety aspects of nuclear waste management can be viewed on two levels: (1) from a macrosystem standpoint, which encompasses the safety aspects concerning the general health and environmental quality of the world community, and (2) from the microsystem concept, which deals with the safe management of nuclear waste within the reprocessing and waste facilities.

Risk considerations play an instrumental role in determining policy on waste handling techniques especially in the macrosystem. "Risk" is defined as "the probability of radionuclide release times the consequence." Measurement and quantitative expression are complicated by whether a risk is voluntary or involuntary, individual or group focused, current or projected, chronic or catastrophic. A flow chart that depicts the calculation procedures involved in risk analysis is provided in Figure 23-7-6.

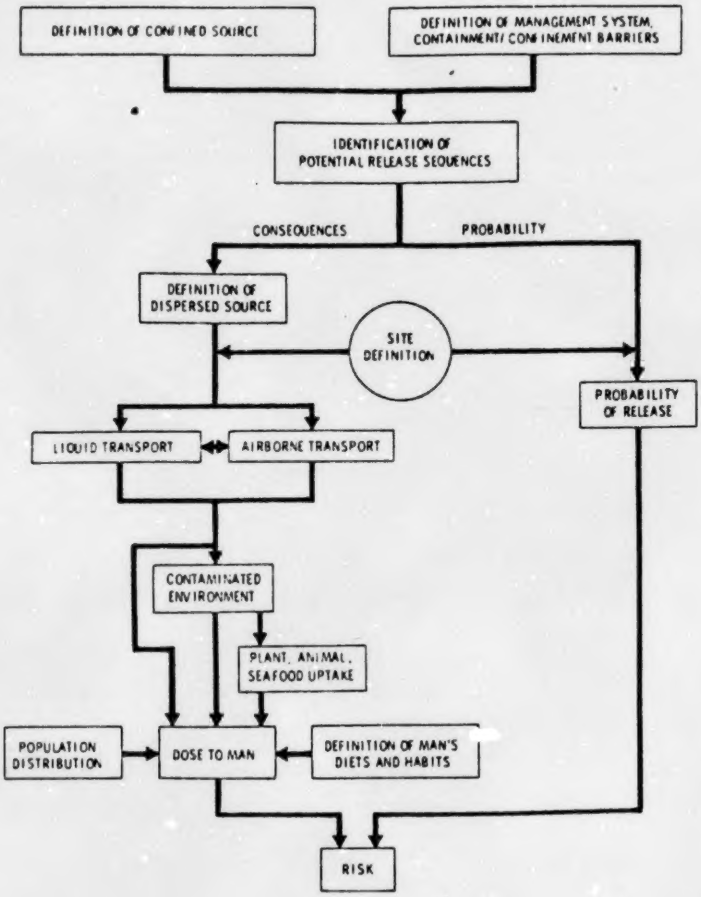
DEFINITION OF CONFINED SOURCE
DEFINITION OF MANAGEMENT SYSTEM, CONTAINMENT/ CONFINEMENT BARRIERS
IDENTIFICATION OF POTENTIAL RELEASE SEQUENCES
CONSEQUENCES
PROBABILITY
DEFINITION OF DISPERSED SOURCE
SITE DEFINITION
PROBABILITY OF RELEASE
LIQUID TRANSPORT
AIRBORNE TRANSPORT
CONTAMINATED ENVIRONMENT
PLANT, ANIMAL, SEAFOOD UPTAKE
POPULATION DISTRIBUTION
DOSE TO MAN
DEFINITION OF MAN'S DIETS AND HABITS
RISK

Figure 23-7-6. Flow chart of risk analysis decisions.

Present programs in the U.S. for high-level wastes are aimed at isolation in deep geologic formations. Risk then is assessed by the different events that could affect the geologic integrity of the isolation and the adverse consequences upon the surrounding environment. Four general causes of breaches in the isolation of wastes have been determined:

- Sudden natural events (i.e., meteorite impact).
- Geologic processes (faulting or ice ages).
- Changes in local geology caused by high radiation or thermal release of wastes.
- Human involvement (sabotage).

The potential consequences of geologic disposal can be calculated with a hazard index. A typical Relative Hazard Index (RHI) is defined for any radionuclide (i) by Equation 23-7-1.

$$(\mathrm{RHI})_i = \frac{Q_i}{(\mathrm{MPC}_w)_i}$$

Equation 23-7-1
(Equation = Eq.)

where:

Q_i = the radioactivity in curies of the radionuclide.

$(\mathrm{MPC}_w)_i$ = the maximum permissible concentration, in curies/m^3, of radionuclide i in drinking water.

The total RHI is the sum of the RHI_i's in the event that several nuclides are released.

Several factors are not taken into account by the RHI, including the inability to take into account the waste form and insolubility, the storage facility design, the location of the nuclides in relation to man's environment, food chain buildup (biological magnification), and the pathway to the water supply.

After initial treatment of the liquid, gaseous, and solid waste streams, the fission products are reduced to calcined solids, inert forms (concrete or glass), a liquid sludge (consisting of salts and an insoluble component), and gases — all of various levels of radioactivity. The different levels of wastes are managed in diverse ways.

Direct discharge of effluents into the environment is limited by the maximum permissible concentration (MPC) of the nuclide and its discharge environment. MPC for air (MPC_a) and for water (MPC_w) refers to the highest concentration of a radionuclide permissible for release without further steps to reduce exposure. However, the concentrations must have been reduced to as low a level as is reasonably achievable. These concentrations are established by the Federal government and are defined in 10 CFR 20. The MPC for air and water for common nuclides are listed in Table 23-7-7.

Intermediate-level wastes of relatively short half-lives may be confined for a period of time in order to allow for decay.

High-level wastes with relatively long half-lives must be isolated from the biosphere for long periods. High-level liquid wastes are stored in acid solutions contained in stainless steel tanks. Those waste streams generated in alkaline form (solvent washers, scrubbers, etc.) are stored in carbon steel tanks. Decontamination of the process equipment is achieved by high pressure jets, agitated baths, or ultrasonic techniques.

TABLE 23-7-7.

MPC FOR AIR AND WATER FOR COMMON FISSION PRODUCTS.

Fission Product	Maximum Permissible Concentration	
	MPC$_w$(water)	MPC$_a$(air)
	Ci/c^3	Ci/c^3
Hydrogen-3	0.03	2×10^{-6}
Chromium-51	0.02	8×10^{-7}
Iron-55	8×10^{-3}	3×10^{-7}
Cobalt-58	10^{-3}	3×10^{-7}
Manganese-54	10^{-3}	10^{-8}
Zirconium-95	6×10^{-4}	10^{-8}
Iron-59	5×10^{-4}	2×10^{-8}
Nickel-63	3×10^{-4}	2×10^{-8}
Cobalt-60	3×10^{-4}	3×10^{-9}
Barium-140	2×10^{-4}	10^{-8}
Cesium-137	2×10^{-4}	2×10^{-8}
Phosphorus-32	2×10^{-4}	2×10^{-8}
Cerium-144	10^{-4}	2×10^{-9}
Strontium-89	10^{-4}	10^{-8}
Cesium-134	9×10^{-5}	4×10^{-9}
Iodine-131	2×10^{-5}	3×10^{-9}
Strontium-90	4×10^{-6}	4×10^{-10}
Uranium-233	4×10^{-5}	4×10^{-11}
Plutonium-239	5×10^{-5}	6×10^{-13}

Combustible solid waste is incinerated to reduce the volume being stored and is converted to a more inert (less reactive) form. Incineration facilities include equipment for preparation of the waste for incineration, the actual incineration, encapsulation of the ash, and off-gas handling equipment.

To prevent exposure to radioactivity in nuclear plants, several design considerations are applied. A waste management plan must take into account pressure differences between areas that contain different radioactivity levels in order that leaks always will be directed from low-hazard levels to high-hazard levels.

Remote handling devices (mechanical processing equipment) for the unloading, storage, and processing of high-level waste, such as spent fuel rods, reduce exposures to workers.

Effluent and environmental monitoring is an important phase of the safety aspects for any waste-handling facility. A continuous monitoring program should be implemented and maintained to measure not only offsite, but onsite, exposure in the form of direct radiation, breathing air, deposited radioactivity, and radioactivity in consumable materials (water, milk, fruit, vegetables, grain, fish, etc.).

Particulate airborne radioactivity is sampled when air is drawn continuously through high-efficiency asbestos paper filters two inches in diameter.

Gaseous radioiodine is measured with a cartridge of activated coconut charcoal located down line from each paper filter.

Moisture is concentrated from the atmosphere for determination of tritium oxide content. Air is pumped through a silica gel column. The concentration of tritium oxide in the air is calculated from the concentration in atmospheric moisture and from the absolute humidity.

The amount of radioactive materials deposited is determined by the analysis of rainwater that has been channeled through ion-exchange columns. The columns are analyzed by gamma spectrometry for gamma emitters. Alpha and beta nuclide emitters are removed from the column with acid and analyzed by chemical methods.

Water is monitored for radioactive and nonradioactive pollutants. The following factors are determined in an analysis: temperature, pH, alkalinity, dissolved oxygen, sulfide, hardness, conductivity, suspended solids, total dissolved solids, volatile solids, fixed residues, biochemical oxygen demand; and the presence of ammonium, calcium, sodium, iron, aluminum, mercury, chloride, nitrite, nitrate, sulfate, and phosphate. Biological measurements also are made to determine the effects of effluent discharge on plant and animal life.

Mathematical models provide estimates of the effect of radioactive releases upon the environment. Modeling is required because most releases of wastes lead to very low concentrations and may not be detectable by analytical methods. To account for all releases by monitoring techniques alone is difficult, even if all the releases are detectable. Modeling procedures also can take into account hypothetical accidental releases.

CALCULATION OF DECONTAMINATION FACTORS

When further decontamination of liquids is impracticable, dilution may be used to permit release in accordance with the guidelines set down by 10 CFR 20, provided that the concentrations have been reduced as much as is reasonably achievable. The ratio between the activity level of the waste stream and the desired activity level (found in 10 CFR 20), is called the "dilution factor."

EXAMPLE

Given: Fifty gallons of cerium-144, in a liquid waste stream, with a radioactivity level of 10^{-2} µCi/cm^3.

Find: The number of gallons of noncontaminated water required to bring the cerium-144 waste to the maximum permissible level for discharge directly into the environment.

Solution: The MPC$_w$ value for cerium-144 is 10^{-4} µCi/cm^3 (from 10 CFR 20).

The dilution factor then is –

$$\frac{10^{-2}\ \mu\mathrm{Ci/cm^3}}{10^{-4}\ \mu\mathrm{Ci/cm^3}} \quad \begin{array}{l}\text{(activity level),}\\ (\mathrm{MPC_w}\text{ value})\end{array}$$

or 10^2, which equals 100.

Multiply the dilution factor (100) by the gallons (50) of effluent to obtain the volume of water needed to dilute the cerium-144:

$$\text{The volume of water necessary} = 100 \times 50$$

$$= 5{,}000 \text{ gallons of water.}$$

EXAMPLE

Given: Twenty-five gallons of cesium-134 are produced with an activity level of $18 \times 10^{-2}\ \mu\text{Ci/cm}^3$.

Find: The amount of noncontaminated water that must be mixed with the waste stream before it is suitable to be released directly into the environment.

Solution:

$$\text{Dilution Factor} = \frac{18 \times 10^{-2}\ \mu\text{Ci/cm}^3 \text{ (activity level)}}{9 \times 10^{-5}\ \mu\text{Ci/cm}^3 \text{ (MPC}_W\text{ value)}}$$

$$= 2 \times 10^3$$

$$- 2{,}000.$$

$$\text{The volume of water necessary} = 2{,}000 \times 25 \text{ gallons}$$

$$= 50{,}000 \text{ gallons of water.}$$

WASTE STORAGE AND DISPOSAL

The necessity of a safe, isolated waste repository is understandable in view of the half-lives of some of the more threatening fission products. The potency of some of the more long-lived products such as strontium-90, cesium-137, (half-lives of 30 years), and plutonium-239 (half-life of 24,000 years) creates a positive need for a "nuclear garbage can."

Cumulative radioactivity content by the year 2000 is estimated to be more than 50,000 million curies of fission products and 1,000 million curies of actinides. Eighty thousand canisters, one foot in diameter by ten feet in length, are projected for the year 2000; this translates into between 30,000 and 60,000 tons of waste. Because of the long half-lives and possible harmful environmental effects, long-term waste disposal is a very controversial topic, comprised of several alternatives. None of the alternatives, other than burial, are yet feasible, due to incomplete environmental data, technological considerations, or economic infeasibility.

High-level wastes from U.S. reactors and weapons manufacturing are to reside from 1,000 to 3,000 ft (300-900 m) below ground in stable geologic formations. Three major types of formations, salt, crystalline, and agrillaceous (shale and clay) are being considered for waste storage facilities. Of the three alternatives, salt beds seem to be the best choice.

Salt beds offer several advantages over crystalline and agrillaceous formations. There are roughly 50,000 square miles of salt beds in the U.S., and they are located in areas thought to be free of earthquake hazards. The existence of salt has been thought to indicate that there has been no water penetration into the formation, which is an important consideration in terms of wastes leaching into groundwater. However, the possibility of water penetration now is under study. Storage in salt beds is believed by many experts to be the most practical method, especially if the radioactive waste is sealed in strong, retrievable containers. Salt also has a self-sealing characteristic, in that it will flow to relieve heat stress and fuse as it cools. It is also a good radiation shield and dissipates heat better than other types of rock.

Seabed Disposal

Currently, some low-level radioactive wastes are dumped offshore; however, new techniques of seabed disposal are being investigated. The new techniques entail placement of canisters of solidified high-level waste in stable geologic formations in the deep oceans. Although this option appears promising, there is a need for more detailed information on the biological effects of such containment.

Ice-Sheet Disposal

Ice-sheet disposal in Antarctica or Greenland has been suggested as an alternative form of waste disposal. Waste canisters would be allowed to melt, during a period of four or five years, through the ice to the bottom of the ice sheet.

Space Disposal

Disposal into space has been suggested, although it is not now cost effective (over $2,000/kg for a space shuttle transport). The waste package would have to be strong enough to remain intact in the event of a shuttle accident.

Transmutation

Transmutation may convert fission products from long-lived nuclides to shorter-lived elements. The process involves bombardment of the nuclei of the long-lived wastes with photons or subatomic particles. This procedure would involve charged-particle accelerators, nuclear explosions, fission reactors, or fusion reactors.

SUMMARY

Waste treatment facilities process radioactive effluents that are formed directly or indirectly from the fission process. The resulting waste streams – solid, liquid, and gaseous – are treated according to their physical state, combustibility, and radioactivity level. The major concern in a treatment operation is to reduce the radioactivity of the fission products to acceptable levels before they are allowed to enter the environment. The standards are set down in the Code of Federal Regulations, Title 10, Part 20. The longer-lived nuclides, such as the transuranics, are disposed of by decontamination and then burial.

EXERCISES

1. A thousand gallons of process coolant water are contaminated with cesium-137. A factor of 10^4 decontamination is needed to allow recycle of the water. Conductivity of the coolant water shows a very low percentage (less than 0.01 percent) of dissolved solids. What is a practical method for decontamination of the waste?
2. In the manufacturing process for making uranium oxide pellets for reactor fuel, one ton of pellets have been made, but do not meet specifications. Is it better to reclaim the uranium's value or to let this material be waste? Devise a simple flowsheet for the recovery of the uranium by dissolution of the uranium oxide in nitric acid.
3. What is the maximum permissible concentration in water that is allowed for uncontrolled release for the following isotopes:
    a. Plutonium-239.
    b. Americium-241.
    c. Radium-226.
    d. Strontium-90.
    e. Cesium-134.

MATERIALS

1	25-ml beaker.
1	400-ml beaker.
1	25-ml wash bottle.
1	25-ml analytical buret with stopcock.
15	10-ml counting vials.
1	50-ml funnel.

1 drop buret.

1 well type γ counter with NaI detector.

1 glass wool plug.

1 vertical support bar.

1 clamp.

250 ml of 0.25-M inactive $La(NO_3)_3$ – (Dissolve 20.30 g of $La(NO_3)_3$ in distilled water to make 250 ml of solution).

*** ml of La-140 tracer solution – (La-140, t ½ = 40.3 hr, E = 2.5 MeV).

5 g Dowex-50 cation resin (crosslinkage 8%).

*** See Instructor as to volume of La-140 tracer to be added.

PROCEDURES

1. Prepare resin column as illustrated in Figure 23-7-7.
    a. Place glass wool plug in bottom of the 25-ml buret.
    b. In a 25-ml beaker, slurry 5.0 g of resin in water. (Use approximate 8 ml of water.)
    c. Transfer the slurry in b to the 25-ml buret.
    d. Use the wash bottle to transfer any resin clinging to the side of the 25-ml beaker.
    e. Drain the excess liquid off the buret by opening the stopcock until the water level is slightly above the resin.
    f. With a clamp, attach the buret to the vertical support bar.

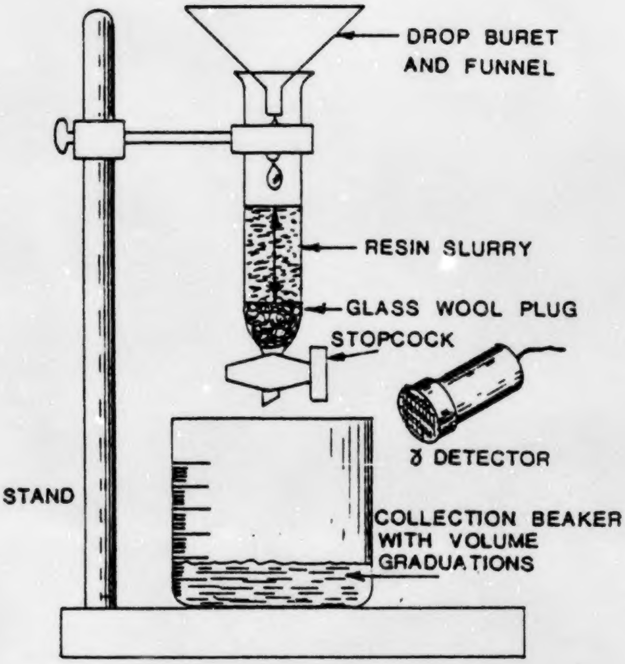
DROP BURET AND FUNNEL
RESIN SLURRY
GLASS WOOL PLUG
STOPCOCK
γ DETECTOR
STAND
COLLECTION BEAKER WITH VOLUME GRADUATIONS

Figure 23-7-7.
Laboratory resin column
and γ detector.

2. Add the La-140 tracer to the 250-ml solution of 0.25 M $La(NO_3)_3$ to give approximately 104 cpm/ml. (See Instructor as to the volume of the La-140 tracer to be added.)
3. Using the drop buret and the funnel, add the $La(NO_3)_3$ and La-140 solution to the resin column at a rate of approximately 2 ml/min.
4. Collect effluent samples (from the resin column) of approximately 10 ml each in the counting vials, and record the time (approximately 5 min for each vial) in Data Table 23-7-1. Continue collecting samples until 150 ml of the $La(NO_3)_3$ and tracer solution has been used.
5. Count samples collected, using the γ detector.

6. Plot sample activity versus the effluent volume on a graph. The volume at which detectable activity is observed is the breakthrough capacity of the resin column. Make the graph from data in Data Table 23-7-1.
7. When finished, place the solutions in the waste container. DO NOT WASH SOLUTIONS DOWN THE SINK.

DATA TABLE 23-7-1.

Effluent Volume (ml)	Time (min.)	Sample Activity (cpm/ml)
10		
20		
30		
40		
50		
60		
70		
80		
90		
100		
110		
120		
130		
140		
150		

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TEST

1. Match each term in column A with a definition in column B, by placing the correct alphabetical letter in the parentheses.

Column A

Low-level waste. (____)

Intermediate-level waste. (____)

High-level waste. (____)

Calcination. (____)

Evaporation. (____)

Ion exchange. (____)

Relative Hazard Index. (____)

Maximum Permissible Concentration. (____)

Decontamination Factor. (____)

Column B

A. $\frac{Q_i}{(MPC_w)_i}$

B. Reversible exchange between a solid and liquid in which there is no substantial change in the structure of the solid.

C. $\frac{\text{ACTIVITY LEVEL}}{\text{MPC}_w\text{ VALUE}}$

D. Direct discharge of low-level wastes into the environment is dependent upon this concentration.

E. Wastes that originate outside the reactor and are not concerned directly with the nuclear process.

F. Conversion of liquid waste to size 0.05-0.5 mm granules.

G. Waste that has an average activity concentration of a few hundredths of a curie per gallon.

H. Conversion of liquids into a vapor, leaving behind insoluble particles.

I. Wastes that originate from fuel rods and that consist of cesium-137, strontium-90, and iodine-137.

J. Liquid waste management.

K. Phenolic acid groups.

2. Define types and physical forms of radioactive effluents that require waste treatment.

3. Where would you expect to locate the $(MPC)_w$ and $(MPC)_a$ values for neptunium-239?

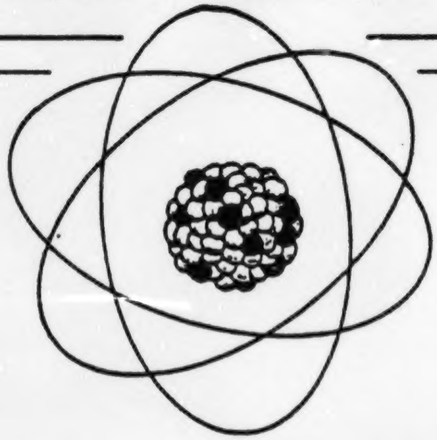
4. What type of filtration is required when a gaseous effluent contains particulates in the range of 0.1 to 1.0 micron?

5. What general technique is employed to remove low levels of ionic radioactive impurities such as cesium and strontium from low-level waste streams such as coolant water?

6. Why are transuranic wastes placed in a separate category?

7. Spent resin, slightly contaminated with strontium-90 from a waste treatment facility has lost its exchange capacity and no longer is suitable for use in a waste treatment facility. Describe a general flowsheet for treatment of this resin as a combustible waste.

8. What type of information would you expect to find in the Code of Federal Regulations, Title 10, Part 20 (10 CFR 20)?



NUCLEAR TECHNOLOGY

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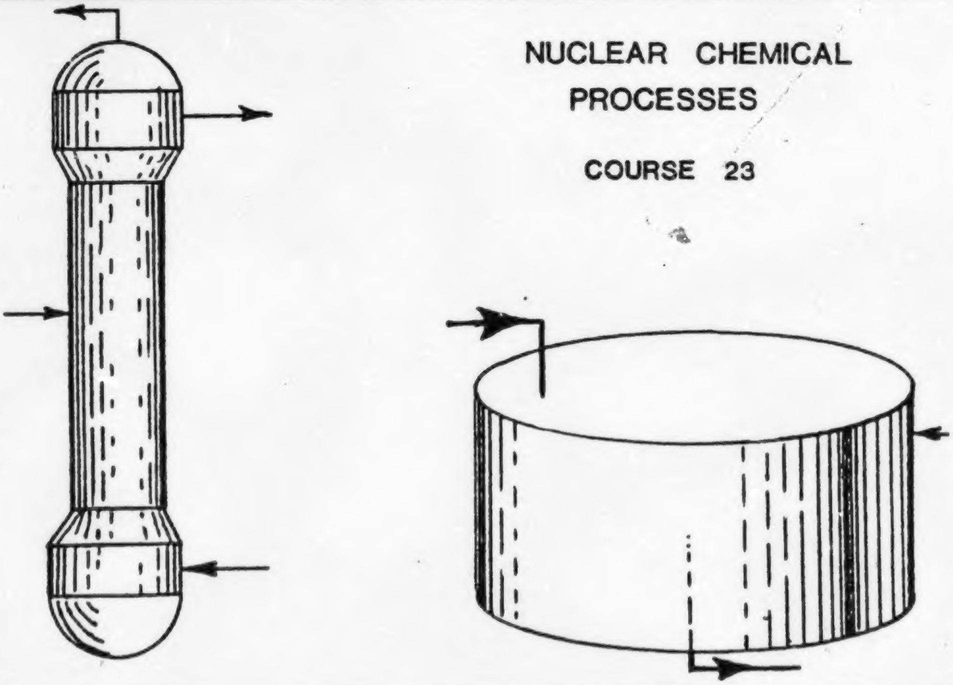
COURSE 23 - NUCLEAR CHEMICAL PROCESSES



NUCLEAR CHEMICAL PROCESSES

COURSE 23

CORD CENTER FOR OCCUPATIONAL RESEARCH AND DEVELOPMENT

NUCLEAR TECHNOLOGY SERIES
INDEX
for
COURSE 23, NUCLEAR CHEMICAL PROCESSES (SEVEN MODULES)

NOTE: Each module in this Course is numbered separately, and the page numbers begin with page 1 in each module. Therefore, this Index lists for each entry the module number (underlined), followed by a comma and the page number. Figures and tables are listed by their numbers, followed by the module and page number in parentheses. A Master Index is available in a separate volume. This general index merges all index entries from the 35 Nuclear Courses. It is a valuable research tool, with which the student or researcher can locate all the references to any subject within the 35 Courses.

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